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TRANSLITERATION

There is no ideal system of transliterating Russian; each has its advantages and disadvantages. For the translation of Geokhimiya we have chosen the system used by Chemical Abstracts, partly because of its wide acceptance by other journals and partly because of certain advantages in alphabetization of names. The principal differences between this system and others in common use are as follows:

Russian	Chem. Abs.	Others
Х	kh	h
Ц	ts	tz
Щ	shch	sch
Ю	yu	iu
Я	ya	ia

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ISOTOPE FRACTIONATION OF ATMOSPHERIC OXYGEN

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A direct determination of the isotopic composition of oxygen produced by otosynthesis in plants, made by us some time ago, showed that photosyn- etic oxygen is a result of dissociation of water [1] and is lighter than at- ospheric oxygen. The question arose at that time, why atmospheric oxy- n should be heavier if photosynthetic oxygen is its main source. The otopic composition of oxygen from different sources, based on numerous alyses, is presented in Table 1.

After it was established that photosynthetic and atmospheric oxygen do t have the same isotopic composition, the hypothesis was advanced that nospheric oxygen is heavier because of fractionation of the oxygen iso- es by oxidation and respiration of plants and animals and preferential ation of the lighter isotope, O^{16}, during these processes. This phe- menon is characteristic of the kinetics of isotopic molecules (arising m the difference in the O^{18} -- O^{18} and O^{16} -- O^{16} bonding energies).

Numerous experimental investigations have been made in order to deter- ne the fractionation factor of oxygen for the process of respiration of nts and animals and for oxidation of organic matter under natural condi- ns. The most systematic of these investigations are those of Dole and s associates [3]. On the basis of data from a single station, Rakestraw al. [2] reported at first that a very strong enrichment in the heavy oxy- n isotope, amounting to 7 γ, results from the oxidation of organic matter nd the respiration of organisms) in the sea. Later, using data from four tions in the Pacific Ocean, Dole and his co-workers [3] reported that the ctionation factor for the absorption of oxygen dissolved in sea water is .991. Finally, in his last work, Dole [4] showed that the fractionation tor for the respiration of plants and animals ranges from 1.008 to 1.029. concluded that it is precisely this process that enhances O^{18} content in otosynthetic oxygen by preferential removal of the lighter isotope.

Our investigations of the isotope fractionation in the oxygen of soils and an water and the refinement of data on the isotopic composition of photo- thetic oxygen have led us to a different conclusion concerning the causes he difference between the isotopic composition of photosyntehtic and nospheric oxygen.

Table 1

Source of oxygen		Amount in tons	$\%O^{18}$	ΔO^{18} % as compared with fresh water	ΔO^{18} in γ as compared with fresh water
Atmosphere		$1 \cdot 10^{15}$	0.2039	2.92	6.5
Photo-synthesis	fresh-water	$5 \cdot 10^{10}$	0.1991	0.54	1.2
	marine	$2.2 \cdot 10^{11}$	0.2005	1.21	2.7
Hydro-sphere	oxygen dissolved in water	$8 \cdot 10^{12}$	-	-	-
	fresh water	$2.1 \cdot 10^{16}$	0.1981	0.0	0.0
	sea water	$1 \cdot 10^{18}$	0.1995	0.67	1.5
Atmospheric carbon dioxide		$1 \cdot 10^{12}$	0.2083	5.15	11.5

EXPERIMENTAL SECTION

1. Method of Determination of the Isotopic Composition of Oxygen.

The determination of the isotopic composition of oxygen was made on the two-beam mass spectrometer MO-2 by the null-point method. The measurements were made on peaks 34 and 32 (corresponding to the isotopic molecules $O^{16}O^{18}$ and $O^{16}O^{16}$). Both beams were received simultaneously by two receivers, amplified and passed on to the null-point system.

The measurements were made by comparing the isotope ratios in standard oxygen and in the sample. The inlet system included a 1200 ml buffer vessel, a leak 30 μ in diameter, an inlet valve and a valve for opening sample ampoules. The gases were admitted to the spectrometer alternately at intervals of 2 to 3 minutes by means of four electromagnetic valves [5]. The difference in the isotope ratios was determined by the formula:

$$\delta^0/_0 = \frac{(O^{16}O^{18}/O^{16}O^{16})_{sp.} - (O^{16}O^{18}/O^{16}O^{16})_{std.}}{(O^{16}O^{18}/O^{16}O^{16})_{std.}} \cdot 100$$

The error of measurement amounted to $\pm$ 0.03 — 0.05% relative to a standard of atmospheric oxygen taken in a suburban locality on the leeward side. It should be noted that atmospheric oxygen from an open place has constant isotopic composition adopted by the International Bureau of Standards

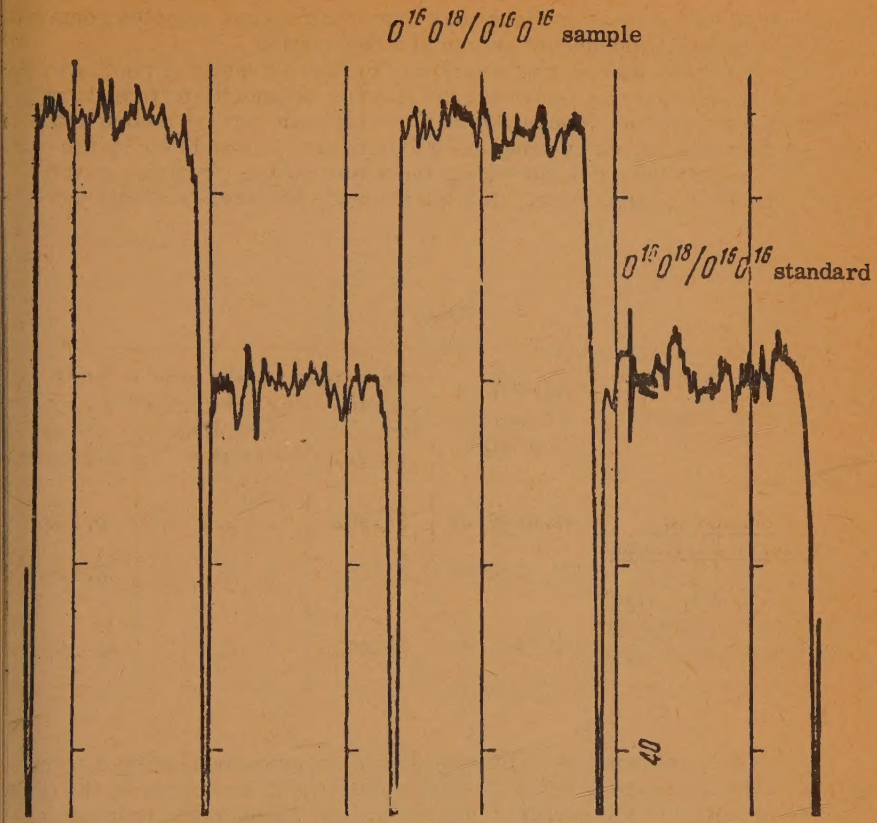

Fig. 1. Mass spectrogram. Peaks 34 and 32

as standard. In a special investigation [3] it was proved that the isotopic composition of atmospheric oxygen at different points on the earth is exactly the same up to altitude of 80 km. Only the $O^{18}:O^{16}$ ratio is usually considered, because the content of the third isotope, O^{17}, is negligible. Therefore, when we discuss the isotopic composition of oxygen (photosynthetic, in sea water, etc.), we imply the isotopic ratio $O^{18}:O^{16}$.

2. Isotopic Composition of Photosynthetic Oxygen.

To determine the isotopic composition of photosynthetic oxygen produced by marine phytoplankton (this value being previously computed theoretically), experiments were made with diatoms at the Sevastopol' biological station (Black Sea); and for refining the isotopic composition of freshwater photosynthetic oxygen, determinations were made on the higher plant Elodea canadensis.

In the experiments with Elodea canadensis, samples of photosynthetic

oxygen were collected after discarding numerous oxygen samples contaminated by residual atmospheric oxygen and respiration.

In the work with marine phytoplankton, the low intensity of photosynthesis made it necessary to determine the isotopic composition from the difference in the isotopic composition of photosynthetic oxygen before and after photosynthesis, calculating the intensity of photosynthesis by the Winckler method and decontaminating the water containing diatoms completely in a special apparatus. Table 2 presents the results of this work.

Table 2

Species of plant	ΔO^{18} in % of content in air	$\%O^{18}$ in photo-synthetic oxygen	ΔO^{18} in γ as compared with fresh water	$\%O^{18}$ in water of the experiment
Elodea canadensis	-2.34±0.04	0.1992	1.2	0.1981
Chatocerus curvisetus Chatocerus Lauderi Nitzschia closterium	-1.99±0.03	0.1999	2.0	0.1993
Skeletonema costatum Chatocerus curvisetus	-1.72±0.03	0.2005	2.6	0.1993

The isotopic composition of photosynthetic oxygen produced by marine phytoplankton (average $\%\ O^{18} = 0.2002$) was found to be nearer to the isotopic composition of the oxygen of sea water than indicated by theoretical calculations [4].

Evidently, the actual isotopic composition of photosynthetic oxygen is identical with the isotopic composition of oxygen in water, the observed difference being the result of enrichment of photosynthetic oxygen in the heavier isotope due to respiration resulting in preferential fixation of O^{16} (to be discussed in greater detail in a separate paper).

3. Isotope Fractionation of Atmospheric Oxygen in Soil.

To investigate the possible isotope fractionation of oxygen during the processes of respiration and oxidation in soil, we made isotopic analyses of soil air taken from different horizons (20, 40, 80 and 100 cm) of typical soils in the Main Botanical Garden, in the Ukraine, on Kola Peninsula and in the region of Sukhumi (Caucasus). In most cases no isotope fractionation was detected and the occasional variations in the composition of oxygen for which α averaged 0.997, always coincided with excessive moisture in the soil. This work is described in detail in a separate paper.

Stations at which oxygen samples were taken.

Asterisks indicate stations for which the determination of the isotopic composition of oxygen has been completed.

4. Isotope Fractionation of Atmospheric Oxygen in the Ocean.

In the depths of the ocean the oxygen dissolved in its waters is continuously absorbed as a result of oxidation of organic matter and respiration of organisms. It was desirable to determine the isotopic composition of the oxygen remaining in solution.

Samples of oxygen dissolved in sea water were collected during the second voyage of the Marine Antarctic Expedition on the "Ob'". The samples were taken at the stations marked with the asterisk on the map, the sampling horizons (in the vertical section from surface to bottom) being so

Table 3

No. of station	Depth in meters	ΔO^{18} in % of atmospheric oxygen	Amount of O_2 in ml/l	Value of α absorption	Temperature, °C
	0	0,0	7,82	—	1,09
210	1140	0,45±0,04	4,56	0,992	1,46
	0	0,0	8,40	—	—
	100	0,12±0,04	7,57	0,989	0,70
	1099	0,60±0,04	4,85	0,990	0,70
237	3184	0,58±0,03	5,54	0,986	—0,23
				α_{av}=0,988	
	0	0,0	8,22	—	0,03
	98	0,16±0,03	6,90	0,993	—1,03
246	362	0,54±0,03	5,09	0,989	0,62
	2970	0,45±0,03	5,49	0,939	—0,20
				α_{av}=0,990	
	0	0,0	5,95	—	15,96
257	1951	0,39±0,08	4,81	0,982	2,65
	0	0,0	6,86	—	7,95
	100	0,06±0,03	6,93	—	6,10
269	400	0,27±0,02	5,71	0,988	4,21
	939	0,37±0,02	4,55	0,992	2,92
	1814	0,30±0,03	4,60	0,992	2,52
				α_{av}=0,990	
	0	0,0	6,89	—	6,67
	100	0,11±0,03	6,86	—	6,56
291	800	0,11±0,02	5,05	0,996	2,12
	3200	0,51±0,03	4,91	0,985	0,78
				α_{av}=0,990	
	0	0,0	4,59	—	29,0
314	1029	0,80±0,04	1,81	0,994	5,32
	5100	0,00±0,04	4,52	—	1,16
	0	0,0	4,46	—	29,3
	25	0,00±0,03	4,36	—	29,3
316	100	0,51±0,02	2,42	0,992	22,49
	400	0,52±0,02	2,09	0,995	10,05
	1000	0 58±0,05	1,47	0,995	6,11
				α_{av}=0,994	
	0	0,0	4,50	—	28,9
	25	0,19±0,03	4,58	—	28,9
327	100	0,36±0,03	0,25	0,998	19,47
	750	0,92±0,04	0,48	0,996	8,08
	1500	0,80±0,03	1,87	0,992	4,10
				α_{av}=0,995	

Note: Comma represents decimal point.

selected as to include oxygen minima, i.e., those places in the ocean where the amount of oxygen expended in the oxidation of dissolved organic matter and in respiration of organisms was the greatest. The water from the bathymeters was quickly siphoned off into a system where it was degassed, and the liberated gases were sealed in ampoules. The results of mass-spectrometric analyses of the samples are given in Table 3.

The value of $\alpha_{abs.}$ was computed by the well known formula [3]:

$$(\alpha_{abs.} - 1) \ln \frac{c_2}{c_1} = \ln \frac{y_2}{y_1}$$

where $\alpha_{abs.}$ is the fractionation factor of absorption;

c_1 and c_2 are the initial and final concentrations of oxygen in water;

y_1 and y_2 are the initial and final amounts of O^{18} in the dissolved oxygen.

The factor $\alpha_{abs.} = \frac{\%O^{18} \text{ absorbed}}{\%O^{18} \text{ remaining}} < 1$. In discussing the enrichment of atmospheric oxygen in the heavy isotope, it is convenient to use the reciprocal of the above ratio: $\alpha = \frac{1}{\alpha_{abs}} = \frac{\%O^{18} \text{ remaining}}{\%O^{18} \text{ absorbed}}$. This value corresponds to the general case of enrichment of atmospheric oxygen in O^{18} due to fractionation and the exchange reactions discussed below. The factor α for the isotope fractionation of atmospheric oxygen in ocean water, according to our data, is 1.010 (mean value of $\alpha_{abs.} = 0.990$).

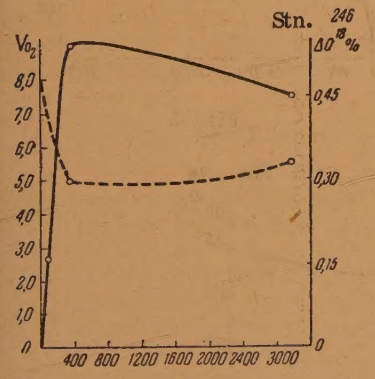

Fig. 2

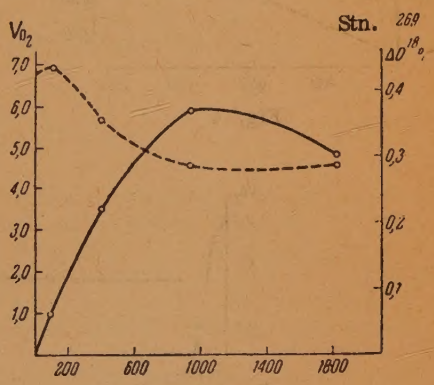

Fig. 3

Note: Comma represents decimal point.

The values of α obtained are typical for the oceans of the entire world, for the investigated waters cover the entire temperature range and all known cases of absorption of oxygen in the ocean (oxygen minima). The observed tendency of α to increase with decreasing temperature is typical

for isotope fractionation. This phenomenon evidently explains the wide scatter in the results of Dole and co-workers [3], who did not take into consideration the hydrochemical characteristics of the region they investigated.

All the surface samples we analyzed indicate that the isotopic composition of oxygen dissolved in ocean water is the same as for atmospheric oxygen, owing to intensive aeration and mixing of surface waters. The oxygen minimum in ocean water always coincides with the greatest enrichment of the dissolved oxygen in O^{18}. This is shown by the graphs of Fig. 2 (Stn. 246), Fig. 3 (Stn. 269) and Fig. 4 (Stn. 327). The amount of oxygen in

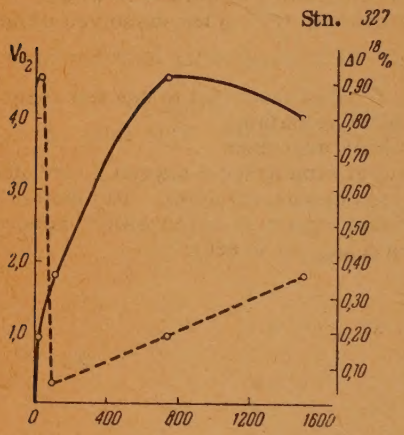

Fig. 4

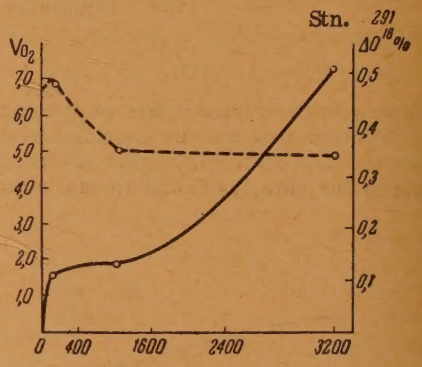

Fig. 5

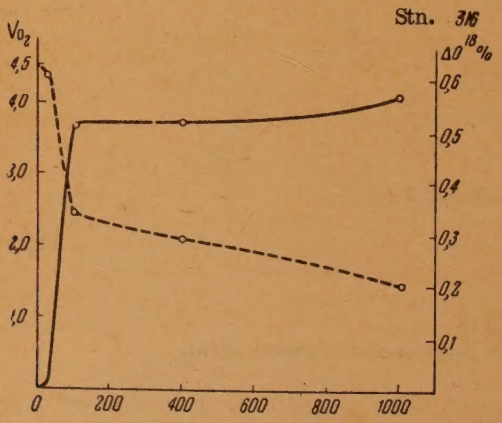

Fig. 6

Note: Comma represents decimal point.

ea water and the degree of its O^{18} enrichment are plotted as the ordinate nd the depth of water as the abscissa. In cases when the oxygen content n sea water does not diminish with depth, or even increases a little after relative decrease, the amount of O^{18} in the dissolved oxygen increases niformly, evidently due to a decrease in water temperature with depth and concomitant increase in the value of α; see Fig. 5 (Stn. 291), Fig. 6 (Stn. 16).

It is interesting that a certain increase in the amount of dissolved oxygen t the depths of 25 m (Stn. 327) and 100 m (Stn. 269, 291) is accompanied y an increase in O^{18} content, indicating that the lowering of the zone of tensive photosynthesis and the absence of rapid vertical mixing of water o not compensate for the fractionation of oxygen by respiration and oxida- on of organic matter.

DISCUSSION OF RESULTS

The data obtained by us on the isotopic composition of photosynthetic xygen produced by the phytoplankton of the Black Sea give the value of 2004 for the average percentage of O^{18} in the photosynthetic oxygen of e ocean for the world, the difference in the isotopic composition of the xygen of "average ocean water" [4] and that of the Black Sea [6] being ken into account. If it is assumed that photosynthesis in the world ocean counts for 80% of the total photosynthetic activity and photosynthesis in nd plants for 20%, then the average isotopic composition of photosynthetic xygen is $0.1992 \cdot 0.2 + 0.2004 \cdot 0.8 = 0.2002$. Therefore, the fractiona- on factor for the distribution of the heavy isotope between atmospheric and otosynthetic oxygen is 1.018.

$$\alpha = \frac{0.2309}{0.2002} = 1.018.$$

Several processes leading to the enrichment of atmospheric oxygen in e heavy isotope are possible: 1) fractionation during oxidation, 2) frac- onation due to respiration of plants and animals, 3) fractionation by the idation of organic matter, 4) exchange reactions with water, 5) increase the weight of atmospheric oxygen as a result of mixing of the oxygen oms from carbon dioxide and stratospheric oxygen induced by ultraviolet diation and electrical discharge.

Calculations show that the oxidation of the elements with variable valence onsuming about 10^8 tons of oxygen per year) is not significant, although in me cases the fractionation factor may possibly reach the value of 1.04.

According to Dole and his associates, the respiration of animals and ants compensates for the addition of light photosynthetic oxygen by pref- rential extraction of the lighter oxygen isotope.

Let us consider their method of calculation.

First, the constancy of the isotopic composition of atmospheric oxygen, was pointed out in reference [7], requires that:

$$N_{end} - N_{start} = \frac{n}{O^{16}_{start}} [\underline{N}_2 - \underline{N}_1] [1 + N_{end}]$$

where N_{end} is the percentage of O^{18} in atmospheric oxygen at the end of a year; N_{start} is the initial percentage of O^{18} in atmospheric oxygen; N_1 is the percentage of O^{18} removed by absorption; N_2 is the percentage of O^{18} in photosynthetic oxygen; n is the number of gram-atoms of oxygen removed from the atmosphere or added to it; and O^{16} is the number of gram-atoms of O^{16} in the atmosphere at the initial moment. Hence the condition for constancy of the isotopic composition of atmospheric oxygen is $N_{end} = N_{start} = O$ if $N_2 = N_1$, and from this follows the equality of the factors of fractionation and "weight increase."

$$\alpha = \frac{N_{atm}}{N_1} = \frac{N_{atm}}{N_2}$$

as well as equality of volumes "n" of the absorbed and liberated oxygen. The last requirement of the calculation, the equality of volumes of photosynthetic and adsorbed oxygen, is not fulfilled, for it is well known that the respiration of land and marine plants accounts for only about 15% of photosynthetic oxygen.

Second, it is known that the effect of the isotope fractionation by bacteria (the main consumers of oxygen for respiration) depends on a physiological factor and in the case of sulfur isotopes, for example, varies from 0 to 2.5% (α = 1.00 — 1.015) [8]. This explains the wide variation in the fractionation factor in Dole's experiments from 1.008 to 1.029 [4]. Therefore, we may not take for comparison with photosynthetic oxygen the arithmetical mean value of α obtained in these experiments, 1.018, i.e. α corresponding to "enriched" O^{18} in atmospheric oxygen.

But even if the idea of compensation of atmospheric oxygen to the steady state of 0.2039% is accepted, the cause of the difference between the isotopic composition of photosynthetic and atmospheric oxygen remains unexplained. We emphasize the fact that respiration does not compensate for the impoverishment of atmospheric oxygen in the heavy isotope by photosynthesis.

More realistic is a calculation based on the data for the isotope fractionation of oxygen dissolved in ocean water by oxidation of organic matter and respiration of organisms. If it is assumed that the fractionation during the absorption of atmospheric oxygen is the only cause of enrichment in the heavy isotope, then this fractionation must occur in a constant volume (since the total amount of atmospheric oxygen is constant and the condition of equilibrium is fulfilled when $N_{atm} = N_o$, where N_o is the initial % O^{18} in the atmosphere, equal to N_{ph} and $N_{abs} = N_{ph}$). The average fractionation factor, as we have shown, is 1.010. Dole obtained practically the same value for 4 stations in the Pacific. Hence, $N_{atm} = N_o \cdot \alpha = N_{ph} \cdot \alpha = 0.2002 \cdot 1.010 = 0.2022$. In other words, absorption of oxygen will maintain the level of the O^{18} content in the atmosphere at 0.2022% and not at 0.2039% as in the present day atmosphere. Thus, even this large-scale process in the ocean does not compensate for photosynthesis and is not responsible for the present composition of atmospheric oxygen.

The above-mentioned isotope exchange reaction between oxygen and water

1. $O_2^{16} + 2H_2O^{18}$ (g) $\rightleftarrows O_2^{18} + 2H_2O^{16}$ α = 1.017 (0°C), 1.014 (25°C)

2. $O_2^{16} + 2H_2O^{18}$ (l) $\rightleftarrows O_2^{18} + 2H_2O^{16}$ α = 1.006 (0°C), 1.006 (25°C)

nay be considered as a secular process. Judging by the constancy of the sotopic composition of oxygen in the ocean for the world, the exchange is extremely slow and rapid fluctuations are evidently not regulated by it. The present isotopic composition of atmospheric oxygen does not correspond to the equilibrium:

$$\%O^{18}_{(equil.)} = O^{18} \text{ (in water)} \cdot \alpha = \begin{cases} (1)\ 0.2028 \text{ instead of } 0.2039 \\ (2)\ 0.2006 \quad " \quad \text{of } 0.2039 \end{cases}$$

We turn now to the possibility of enrichment of atmospheric oxygen in the heavy isotope at the expense of the carbon dioxide oxygen containing 0.2083% O^{18}, as the result of mixing of atoms and ions of oxygen according to the reactions:

Photochemical	Ionization
$O_2 \xrightarrow{h\nu} O + O$	$O_2 \rightarrow O + O^+ + \underline{e}$
$CO_2 \xrightarrow{h\nu} CO + O$	$CO_2 \rightarrow CO + O^+ + \underline{e}$
$CO \xrightarrow{h\nu} C + O$	$CO_2 \rightarrow CO^+ + O + \underline{e}$

and recombination of "average oxygen" by vertical circulation between stratosphere and troposphere during a limited period of time. Observations on the dynamics of the fragments from atom bomb explosions indicate that approximately 10 years are required for their settling from the stratosphere. We shall take this time as the rate of mixing [9–12].

Let us discuss a hypothetical case in which the absorbed oxygen has the same isotopic composition as photosynthetic oxygen and the total amount of oxygen in the atmosphere is constant.

Then the process of enrichment of oxygen in the heavy isotope is identical to what occurs in a fractionating column with constant level, assuming the amount of vapor to be equal to the amount of oxygen in the stratosphere and the amount of rising vapor to be equal to the amount of absorbed oxygen or the amount of photosynthetic oxygen.

Taking the content of 0.2039% O^{18} in atmospheric oxygen as corresponding to the steady state in the time interval T_0 to T, we have:

$$\underline{N}_{equil.} = N_0 \cdot \alpha^{\underline{p}}, \text{ where } \alpha = \frac{\%\ O^{18} \text{ in the stratosphere,}}{\%\ O^{18} \text{ in the troposphere}} \text{ or } 1.018 = \alpha^{\underline{p}},$$

where $\underline{p}$ is the number of turnover cycles for the total amount of stratospheric oxygen.

Then for CO_2 content amounting to 0.02% and initial isotopic composition of atmospheric oxygen identical with that of photosynthetic oxygen, the time interval $\underline{p}$ needed for the attainment of the steady state in the oxygen isotopic composition of the atmosphere at 0.2039% O^{18} will range from 200 to 500 cycles, since α has a tendency to decrease with increase in the percentage of O^{18} in the atmosphere and varies from 1.0001 to 1.00005. The factor α is calculated from the ratio:

$$\alpha = \frac{A_{O_2} \cdot N_{O_2} + A_{CO_2} \cdot N_{CO_2}}{A_{O_2} + A_{CO_2}} \Big/ N_{O_2}$$

where $\underline{A}_{O_2}$ and $\underline{A}_{CO_2}$ are amounts of atmospheric oxygen and carbon dioxide and N_{O_2} and N_{CO_2} correspond to the percentages of O^{18} in the oxygen and carbon dioxide of the atmosphere.

It is evident and should be stressed that α depends on the concentration of carbon dioxide in the atmosphere and $\underline{N}_{CO_2}$ = const., since it is determined by the exchange equilibrium between carbon dioxide and water.

Assuming that the duration of one cycle is ten years and the concentration of CO_2 in the atmosphere is 0.02%, we get about 5000 years for the time required for the attainment of steady-state, i.e. for the percentage of O^{18} in the atmosphere to reach 0.2309%. This figure has only one meaning: it shows that if the process of mixing of stratospheric and tropospheric oxygen is admitted, then the steady state corresponding to the present day oxygen isotopic composition of the atmosphere is attained in geologically short periods of time.

True, this calculation was made disregarding the fact that the adsorbed and the photosynthetic oxygen differ in isotopic composition. If the isotope fractionation of atmospheric oxygen during absorption is considered, it becomes evident that the "weight increase" of the atmospheric oxygen to the O^{18} content of 0.2022% is accelerated and that afterwards the general balance depends on the ratio of the rates of the following two processes:

a) "decrease in weight" at the rate: $\underline{A}_{ph}\ (\underline{N}_{abs} - \underline{N}_{ph})$, where

$$\underline{N}_{abs} = \frac{\underline{N}_w}{\alpha} = 0.2018 > \underline{N}_{ph}$$

b) "increase in weight" at the rate $A_{atm}\ (\underline{N}_{st} - \underline{N}_w)$, where $\underline{A}_{atm}$ is the amount of oxygen received from the stratosphere per year, assuming its amount in the stratosphere to be $\sim$15% of the total weight of the atmosphere, i.e.

$$\underline{A}_{atm} = \frac{A_w \cdot 15}{100 \cdot 10}$$

Equilibrium is reached when

$$\underline{A}_{ph}\left(\frac{\underline{N}_w}{\alpha} - N_{ph}\right) = \underline{A}_{atm}\ (\underline{N}_{st} - \underline{N}_w)$$

Inasmuch as all values except N_{st} are known and

$$N_{st} = \frac{\underline{A}_{O_2} \cdot N_{O_2} + \underline{A}_{CO_2} \cdot N_{CO_2}}{\underline{A}_{O_2} + \underline{A}_{CO_2}}$$

depends on the concentration of CO_2 in the atmosphere, the concentration of CO_2 must be of the order of 0.1%

Thus the CO_2 content in the present day atmosphere, together with isotope fractionation of oxygen during absorption, do not suffice to compensate for the introduction of the lighter photosynthetic oxygen by the method described above. Calculations show that this requires $\sim$0.1% CO_2 in the atmosphere. It is true that the mass-spectrometric method is not precise

nough at present to register slight variations in the oxygen isotopic composition of the atmosphere. Calculations show that the "weight decrease" of atmospheric oxygen produced by photosynthesis alone over a period of) years, without any fractionation processes, would be within the limits of perimental error.

Assuming that the enhancement of atmospheric oxygen in the heavy isope is the result of the averaging of the isotopic composition of free oxygen the stratosphere, it may be concluded that the composition of atmospheroxygen is a function of the carbon dioxide content in the atmosphere. his means that it is theoretically possible from the isotopic composition of ygen in ancient oxides to determine the carbon dioxide content in the atosphere at different periods in the history of the earth.

Summary

1. The fractionation factor α for the isotope fractionation of atmospheroxygen in the ocean is 1.010, while the fractionation of oxygen in soil due the increase in soil moisture is negligible.

2. The magnitude of the isotope fractionation of atmospheric oxygen in e ocean and in soil is not sufficient to explain the difference between the otopic composition of photosynthetic and atmospheric oxygen.

3. We believe that the oxygen isotopic composition of the atmosphere is function of the CO_2 content and varies with its concentration in the atmosere. Hence, the isotopic composition of oxygen in ancient oxides prodes a means of estimating the concentration of carbon dioxide in the atosphere at different periods during the history of the earth.

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DISTRIBUTION OF MANGANESE IN SEDIMENTARY ROCKS

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1. INTRODUCTION

Information concerning sedimentary deposits of a number of chemical elements (Al, Fe, P, Mn, U, etc.) exceeds by many times our knowledge about their distribution clarkes in sedimentary rocks. This disproportion in information is particularly noticeable in the case of manganese. Owing to work done by A. G. Betekhtin [5, 6, 7], V. I. Vernadskii [8, 9], N. M. Strakhov [34], N. S. Shatskii [43], Hou Te-feng and Jen Lien-tsun [42], F. Ya. Anosov and I. I. Ginzburg [2], and many other geologists, regional regularities in the distribution of manganese deposits have been established, their relation in time to specific facies and rock formations has been shown, the mineralogical and geochemical zonation of the deposits has been studied, the paragenesis of manganese with other elements in ores has been examined, etc. In contrast to this there is only fragmentary and not always sufficiently reliable information about the clarke distribution of manganese in sedimentary rocks. The literature on this question is extremely poor. The existing analyses do not give a clear presentation of manganese distribution in sedimentation basins and make it possible to describe individual, relatively small areas in terms of short intervals of the stratigraphic column only in a rough way. The number of manganese determinations in the rocks is quite small in most cases [18, 19, 33, etc.].

The first attempt to elicit regularities in the facies distribution of disperse manganese (and a number of other elements) in sediments in humid zone sea basins was due to N. M. Strakhov and his collaborators [35, 36, 37, 38]. It depended on the results of a joint chemical and lithologico-facies study of the lower Frasnian and the lower Carboniferous deposits of the Second Baku. Because of the inadequacy of the analytical data for a direct elucidation of the regularities in the distribution of manganese in sediments in the area or a cross-section of an ancient basin from its shores to the central portion, N. M. Strakhov used an indirect method to solve the problem. In fact, he postulated that the series of rocks starting with the sands and going through the silts, clays and marls to the limestones

reproduces the whole range of gradual transitions from nearshore facies to the pelagic facies which characterize the central areas of basins. Consequently, by determining the manganese (or some other element) in each type of rock in the series that was mentioned, N. M. Strakhov considered that he had determined the change in the amount of this element in the facies cross-section from the shore to the basin's center. Thus, a gradual increase in the manganese content of the above-mentioned series of rocks from the sands to the limestones was established for the lower Frasnian and the lower Carboniferous rocks of the Second Baku. By interpreting these data by the method that had been adopted, N. M. Strakhov concluded that the amount of manganese dispersed in the sediments inside the basin increases in porportion to the distance from the shore. It reaches a maximum value in the central (pelagic) regions of the basin, that is, at a considerable distance from manganese ore deposits, which it is known are situated along the shores of ancient shallow seas [5, 6, 7, 42].

In this way the paradoxical conclusion is obtained that manganese ore deposits are formed against a background of lower clarkes for this element at the shore end of the facies cross-section. It is possible to doubt the validity of this conclusion immediately since the limestones and clays cannot always be regarded as pelagic sediments, nor the sands and silts as coastal sediments. A vast amount of factual material obtained as a result of drilling for supports in Paleozoic deposits, and in the Devonian of the Russian platform in particular (as well as in other territories), shows that clays and limestones quite often were deposited in the immediate vicinity of the shore, while sands and silts often were disseminated far into the pelagic zone [3]. Such a distribution cannot be considered anomalous since it is far from being accidental and is determined, as was shown by V. V. Belousov [4], by changes in the ratio of raised earth crust to sunken earth crust that occur within the borders of the sedimentation basis and the dry land adjoining it. In addition, currents and other non-wave processes have played a role in the drifting of the sands to a great distance from the shore.

We chose another method for our work and utilized an immeasurably larger amount of analytical material as well as quantitative research methods (mean test samples were prepared, lithologico-geochemical maps drawn, etc.) for the study of the clarke distribution of manganese in sedimentary rocks. Because of the difference in the method of approached used in our constructions and deductions, we depended exclusively on the results from our experimental data. The investigation was conducted by using core samples from support drillings and test wells, and only in the northwestern regions of the Russian platform was supplementary use made of stones from outcroppings. The territory studied in our investigations of the Paleozoic is included within the borders of our maps (Figs. 8 to 10), while more southerly regions, going as far south as the approaches to the Northern Caucasus, were also included in the studies of the Mesozoic and Tertiary deposits.

In most cases individual rock specimens were not analyzed, but mean test samples were prepared from drillings for each stratigraphic interval under study, with sandstone and silts, clay, and carbonate rocks each being considered separately. The methods used in preparing representative mean test samples have been described in other papers [13, 28, 31]. Altogether we tested 410 mean test samples prepared from 6381 specimens from sand and silt deposits, 404 mean test samples prepared from 8883 specimens from clay deposits, and 293 mean test samples prepared from

10389 specimens from carbonate deposits. Besides this, analyses were made of the strata of certain typical cross-sections of coastal and pelagic regions of ancient basins (about 150 analyses). In sum, 25783 rock specimens were included in our investigations, characterizing in various degrees of detail all the geological systems and series (sometimes stages), from the Sinian (Rhipheus) to the Quaternary (Table 1), as well as various lithologico-facies and climatic sedimentation conditions (Table 3). All mean test samples were described by complete silicate and carbonate analyses, the results of which have been published only in part [13, 14, 15, 28, 32].

The manganese was determined by the method that is described below [40]. Rock in the amount of 0.5 grams was treated with 5 milliliters of concentrated HCl and the result was evaporated until dry, after which 20 milliliters of H_2SO_4 (1:4) and five or six drops of 10% H_2O_2 were added and the result was evaporated until there were thick sulfuric anhydride vapors. The amount of manganese in the filtrate was determined colorimetrically. To do this the manganese was oxidized by KIO_4 in a sulfuric and phosphoric acid medium to $HMnO_4$. The intensity of the coloring was measured by a photoelectric colorimeter fitted with a green light filter. The method used makes it possible to determine the amount of manganese in the rocks with sufficient accuracy in the content range from 0.002% to 10.00%. Control experiments which were performed to obtain a comparison with other methods (melting with sodium carbonate, decomposing by hydrofluoric acid [25]) yielded a satisfactory agreement in the results.

Regional changes in the manganese content in the area of a sedimentation basin were studied separately for each lithological type of rock by drawing quantitative lithologico-geochemical maps which were constructed by methods which had been described in other papers of ours [28, 29, 30]. The results of the manganese analyses were plotted on the lithologico-facies background of the maps as circles whose dimensions were made proportional to the number of specimens used in preparing a mean test sample (Figs. 8, 9, 10). In this way the degree of coverage by data of a given region of the Russian platform was depicted on the maps. After the points were plotted on the basic map in correspondence with the distribution of the data, isolines of equal MnO content were drawn for the following values: 0.075, 0.100, 0.150, 0.200, 0.300, and 0.400%. Since the 0.075% isoline nearly corresponds to the mean MnO content in the sedimentary rocks (v. Table 1), by drawing isolines we were able to depict the contours of the regions in which rocks were distributed with negative and positive manganese concentration clarkes for those basin areas of the Russian platform (Givetian and Frasnian) which had been studied.

2. THE DISTRIBUTION OF MANGANESE IN SEDIMENTARY ROCKS OF VARIOUS LITHOLOGICAL CONTENTS AND AGES.

The average manganese content is approximately the same for all the types of rocks considered (Table 1). It is 0.063% in sands and silts, 0.075% in clays, and 0.068% in carbonate rocks. These figures are in direct contradiction to published data according to which the manganese content increases gradually from the sands to the clays and thereupon to the carbonate rocks (Table 2). Such a radical divergence in results compelled us to make a large number of supplementary determinations, but these did

Table 1

Variation in the mean MnO, FeO and Fe_2O_3 content for different types of sedimentary rocks of the Russian platform which are arranged according to the stratigraphic scale

Carbonate rocks	System, series, stage					
	Number of mean test samples	Number of specimens in the test samples	MnO, %	FeO, %	Fe_2O_3, %	Number of mean test samples
nian ((Sn_2)	31	1251	0,105	2,29	2,76	33
ambrian (Cm)	22	394	0,070	1,56	1,89	20
rdovician (O)	14	214	0,064	1,03	2.55	10
otlandian (S)	1	5	0,033	0,72	2,72	6
lurian (O+S)	15	219	0,062	1,00	2,56	16
ower Paleozoic (Pz_1)	68	1864	0,084	1,77	2,45	69
iddle Devonian (D_2)	97	1287	0,057	1,64	2 13	82
erasnian stage (D_3^1)	104	1393	0,070	1,56	2,35	97
amennian stage (D_3^2)	9	117	0,076	1,21	3,40	10
pper Devonian (D_3)	113	1510	0,071	1,53	2,43	110
evonian (D)	210	2797	0,064	1,58	2,29	192
ower Carboniferous (C_1)	21	145	0,021	0,51	2,60	28
iddle Carboniferous (C_2)	15	103	0,072	1,57	2,99	22
pper Carboniferous (C_3)	—	—	—	—	—	—
arboniferous (C)	36	248	0,042	0,95	2,76	50
ower Permian (P_1)	—	—	—	—	—	—
fa stage (P_2^{uf})	7	102	0,083	0 92	2,97	7
azan stage (P_2^{kaz})	5	72	0,069	1,31	2,47	9
atar stage ($P_2^{'at'}$)	9	429	0,075	0,85	3,13	10
pper Permian (P_2)	21	603	0,076	0 99	2,92	27
ermian (P)	21	603	0,076	0,99	2,92	28
iddle and upper Paleozoic (Pz_{2+})	267	3648	0,062	1,45	2,40	270
aleozoic (Pz)	335	5512	0,067	1,51	2,41	339
riassic (T)	5	76	0,094	0,93	4,91	6
ower Jurassic (J_1)	3	21	0,077	1,24	1,68	3
iddle Jurassic (J_2)	7	41	0,100	2,28	1,57	4
pper Jurassic (J_3)	12	62	0,056	2,13	2,51	9
urassic (J)	24+	179	0,069	1,97	2,21	19
ower Cretaceous (Cr_1)	10	111	0,034	2,20	3,82	7
pper Cretaceous (Cr_2)	10	85	0,058	1,32	3,28	4
retaceous (Cr)	20	196	0,043	1,76	3,55	11
esozoic (Mz)	49	451	0,061	1,77	3,03	36
aleocene (Pg)	9	191	0,024	0,95	3,23	11
eocene (Ng)	5	94	0,070	1,31	3,06	7
ertiary (Tr)	17++	314	0,039	1,04	3,27	22+++
uaternary (Q)	9	84	0,043	0,90	2,24	7
enozoic (Kz)	26	398	0,041	0,99	2,91	29
m or mean	410	6361	0,063	1,51	2,52	404

Footnote: All the footnotes below give additional test samples whose age has not been determined ore precisely:
+Two test samples prepared from 55 specimens, J; ++ three test samples prepared from 29 ecimens, Tr; *three test samples prepared from 35 specimens, D_3; **one test sample prepared m 30 specimens, P_2; ***one test sample prepared from 22 specimens, P; ****three test sam- prepared from 74 specimens, J; +++four test samples prepared from 66 specimens, Tr; □ test sample prepared from 81 specimens, Tr.

te: Comma represents decimal point.

Table 1 (Continued)

Sands and silts				Clays					
Number of specimens in the test samples	MnO, %	FeO, %	Fe_2O_3, %	Number of mean test samples	Number of specimens in the test samples	MnO, %	FeO, %	Fe_2O_3, %	Insoluble residue, %
1211	0,115	3,04	4,45	3	106	0,112	1 63	1,41	38,49
557	0,076	2,56	3,93	—	—	—	—	—	—
167	0,061	2,16	2,60	8	473	0,068	0,98	1,08	22,90
531	0,057	2,52	2,67	5	379	0,045	0,87	0,95	21,27
698	0,059	2,29	2,63	13	852	0,057	0,94	1,03	22,27
2466	0,091	2,73	3,89	16	958	0,070	1,07	1,10	25,32
1193	0,069	2,41	4,74	48	783	0,113	1,10	1,19	17,50
2012	0,068	2,18	4,75	84	2768	0,075	0,66	1,19	15,23
266	0,045	1,06	4,41	37	2213	0,021	0,32	0,45	8,78
2313	0,066	2,04	4,72	121	4981	0,056	0 56	0,96	13,26
3506	0,067	2,20	4,73	169	5764	0,075	0,71	1,03	14,46
338	0,028	0,97	4,11	26	814	0,017	0,23	0,59	4,83
250	0,055	1,62	4,60	23	1192	0,021	0,24	0,74	7,46
—	—	—	—	14	520	0,007	0,13	0,51	2,12
588	0,040	1,26	4,33	63	2526	0,016	0,21	0,63	5,19
—	—	—	—	15	715	0,011	0,12	0,41	4,89
91	0,090	1,41	5,73	—	—	—	—	—	—
170	0,103	2,03	3,40	4	66	0,075	0,45	1,13	13,04
404	0,102	0,96	4,78	—	—	—	—	—	—
695	0,097	1,41	4,51	4	66	0,075	0,45	1,13	13,04
717	0,098	1,52	4,51	19	781	0,025	0,19	0,56	6,60
4811	0,068	1,95	4,63	251	9071	0,059	0,55	0,89	11,54
7277	0,077	2,11	4,48	267	10029	0,060	0,58	0,90	12,37
127	0,080	1,06	5,77	—	—	—	—	—	—
17	0,113	4,73	2,12	—	—	—	—	—	—
60	0,088	3,20	1,45	—	—	—	—	—	—
185	0,048	1,78	3,39	8	44	0,142	4,24	4,18	25,48
336	0,071	2,60	2,84	8	44	0,142	4,24	4,18	25,48
179	0,052	2,08	4,32	1	14	0,040	0,41	1,00	12,64
72	0,052	1,44	3,01	6	161	0,027	0,25	1,11	14,23
251	0,052	1,85	3,85	7	175	0,029	0,27	1,09	14,01
714	0,067	2,13	3,64	15	219	0,090	2,39	2,73	20,12
527	0,070	2,30	4,92	7	40	0,093	—	—	23,85
254	0,037	2,05	4,48	3	19	0,248	—	—	21,81
847	0,080	1,97	4,65	11□	140	0,122	0,75	1,51	25,67
45	0,054	0,99	3,31	—	—	—	—	—	—
892	0,074	1,74	4,33	11	140	0,122	0,75	1,51	25,67
8883	0,075	2,09	4,40	293	10389	0,068	0,68	1,02	13,29

Table 2

Comparison of various authors' data for MnO content (in %) of various types of sedimentary rocks.

Rock types	According to N. M. Strakhov et al [38]		According to S. M. Katchenkov and E. I. Flegontova [19]		According to our data					
	Humid zone deposits		Humid zone deposits predominant		Mean for all specimens		Humid zone deposits		Arid zone deposits	
	Number of specimens studied	Mean content	Number of specimens studied	Mean content	Number of specimens studied	Mean content	Number of specimens studied	Mean content	Number of specimens studied	Mean content
Sandstones	7	0.010	30	0.017)	6361	0.063	4101	0.064	2260	0.058
Siltstones	17	0.022	51*	0.055)						
Clays	20	0.052	64	0.075	8883	0.075	6675	0.078	2208	0.067
Carbonate rocks	29	0.147	31	0.120	10 389	0.068	3967	0.105	6422	0.041

*Siltstones and argillaceous siltstones together.

not change the final data of Table 1, thereby confirming the correctness of the values obtained. Attempts were begun to find the reasons for the divergence in the data. Principally they were due to genetic differences between the rocks we had studied and the rocks which had been investigated by the other authors. We subdivided all the types of rocks that had been studied into two genetic types, according to the climatic conditions of their formation: 1) arid, these being formed in a hot and dry climate, and 2) humid, these being deposited in a humid and warm climate. The results of the related statistical calculations are given in Table 3.

The subdividing of the test samples according to the climatic conditions of their formation provided a key to the solution of the problem of the causes for the divergence in the results. It turned out that there are two completely different types of manganese distributions in nature. In humid zone deposits, which were studied by N. M. Strakhov [36, 37], E. S. Tikhomirova [39], and other investigators, the manganese content increases continuously from the sands to the clays and thereupon to the carbonate rocks. But in arid zone deposits the distribution of manganese according to rock types is different. In this case there is a rather small increase in the manganese content from the sands and siltstones to the clays and after that a sharp lowering to the carbonate rocks (v. Table 3 and Fig. 1), the latter type being predominantly dolomites and dolomitic limestones. With a combined statistical treatment of the results, the opposing tendencies in the distribution compensate for each other in the different genetic types, and in consequence there were obtained approximately equal mean contents for manganese in the silts and sands, and the carbonate rocks, and a somewhat higher value in the clays (Table 1).

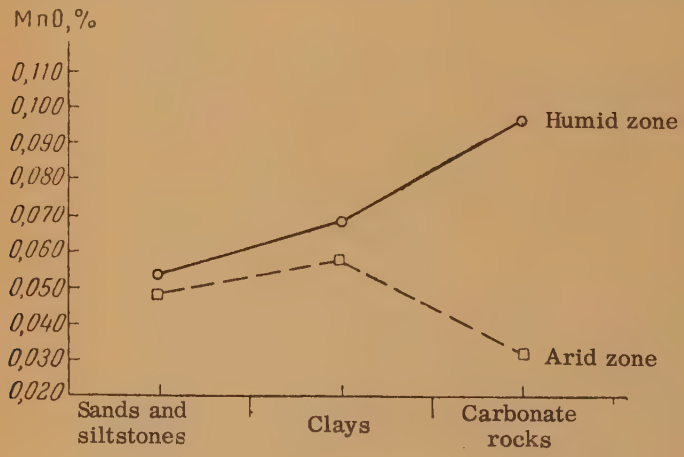

Fig. 1. Variation in MnO content in sedimentary rocks of the Russian platform according to the climatic conditions of their formation (the arid zone according to the data from 390 analyses of mean test samples prepared from 10890 specimens and the humid zone according to the data from 717 analyses of mean test samples prepared from 14743 specimens)

Note: Comma represents decimal point.

Variation in MnO content in sands, clays and carbonate rocks of the Russian platform in relation to the facies and climatic conditions of their formation

Facies conditions	Climatic conditions	Sands and siltstones		
		Number of mean test samples	Number of specimens in the test samples	MnO, %
Continental and lagoon	Arid	97	1676	0.059
	Humid	56	356	0.037
	Sum or mean	153	2032	0.051
Coastal and sea	Arid	10	425	0.058
	Humid	186	2720	0.074
	Sum or mean	196	3145	0.073
Pelagic (open sea)	Arid	8	159	0.052
	Humid	53	1025	0.059
	Sum or mean	61	1184	0.058
All types of facies conditions	Arid	115	2260	0.058
	Humid	295	4101	0.064
	Sum or mean	410	6361	0.063

Table 3 (Continued)

Clays			Carbonate rocks			Mean for all types of sedimentary rocks		
Number of mean test samples	No. of specimens in the test samples	MnO, %	Number of mean test samples	No. of specimens in the test samples	MnO, %	Number of mean test samples	No. of specimens in the test samples	MnO, %
90	1928	0,067	128	4189	0,046	315	7793	0,058
40	480	0,047	—	—	—	96	836	0,041
130	2408	0,061	128	4189	0,046	411	8629	0,053
6	136	0,070	7	204	0,080	23	765	0,068
197	3795	0,087	47	1063	0,150	430	7578	0,088
203	3931	0,086	54	1267	0,141	453	8343	0.087
8	144	0,063	36	2029	0,016	52	2332	0,029
63	2400	0,071	75	2904	0,077	191	6329	0,070
71	2544	0,070	111	4933	0,058	243	8661	0,061
104	2208	0,067	171	6422	0,041	390	10890	0,054
300	6675	0,078	122	3967	0,105	717	14743	0,076
404	8883	0,075	293	10389	0,068	1107	25633	0,068

Note: Comma represents decimal point.

The mean MnO content obtained for all types of sedimentary rocks of Russian platform is 0.068%, or roughly 0.07% (Table 3). In evaluating manganese content we obtain an average distribution for this element in imentary rocks equal to $5.3 \cdot 10^{-2}$%, which is somewhat lower than ?. Vinogradov's estimate ($6.7 \cdot 10^{-2}$%), and is approximately equal to mean Mn content in acidic magmatic rocks ($6.0 \cdot 10^{-2}$%). Since the un Mn content in ultrabasic ($13 \cdot 10^{-2}$%), basic ($22 \cdot 10^{-2}$%), and neutral $\cdot 10^{-2}$%) magmatic rocks is considerably higher [11], while the amount In in ocean water is five times less in order of magnitude and is equal nly $4 \cdot 10^{-7}$% (B10), then the false impression is obtained from the ilable data that the quantitative equilibrium of manganese in the earth's st has been disturbed. In actual fact this is not very probable, since to rmine the equilibrium it would also be necessary to have the facts about distribution of manganese in the world's oceanic sediments and in the osits of the geosynclinal zones in which, apparently, the manganese con- ration is considerably higher than in the platforms. According to A. lervaart's estimate [23], modern oceanic sediments contain approxi- ely four times more manganese than do the sedimentary rocks in plat- ns (0.30% MnO, or correspondingly, 0.23% Mn). If these amounts do change even in the interiors of strata of oceanic sediments, then com- e or partial equilibrium is achieved precisely here. For a definitive tion of the problem it is necessary to obtain data on the distribution of ganese throughout the entire stratigraphic column of the ocean sedi- ts, and study the distribution of manganese in geosynclinal sedimentary ta as well.

The mean percentage content of the manganese varies from the bottom ards along the stratigraphic scale, now revealing epochs of enrichment, revealing epochs of impoverishment for the sedimentary formations of Russian platform in the amount of disperse manganese found in them le 1). The direction of these periodic variations in time is more or the same for all types of rock, but for different intervals there is ob- ed some displacement of the maxima and minima of the curves which acterize the different types of rock (Fig. 2). From this graph it is evident that the smallest amount of variation in the manganese content aracteristic of the sandstones and siltstones, while the greatest varia- is characteristic of the carbonate rocks. The minimal accumulation anganese dispersed in the rocks is found to be in deposits of the middle ods of the Caledonian, Hercynian and Alpine sedimentation cycles (S, r), while the sediments at the beginnings and the ends of these cycles distinguished by considerably higher disperse manganese contents (Sn_2, P_2, T, J, Tr). The majority of the maxima for the curves coincide in with the so-called manganese metallogenic epochs, among whose ber A. G. Betekhtin counts PCm, Cm, D, P_2 and Tr [5, 6, 7], e Hou Te-feng and Jen Lien-tsun list Sn, D, P and Tr [42]. Such a idence can hardly be considered accidental, and it apparently indi- s that the formation of manganese ore deposits proceeded against a ground of general enrichment of sedimentary strata by disperse ganese.

anganese follows iron closely in its distribution along the stratigraphic e. This is quite evident for sandy and clay rocks from the parallelism e curves for the change in manganese and magnetite (Fe_2O_3 + FeO) nt with respect to time (Figs. 3 and 4). The additional curves plotted is chart which show separately the change in the FeO and Fe_2O_3 con- ndicate that for the majority of the time intervals the manganese curve

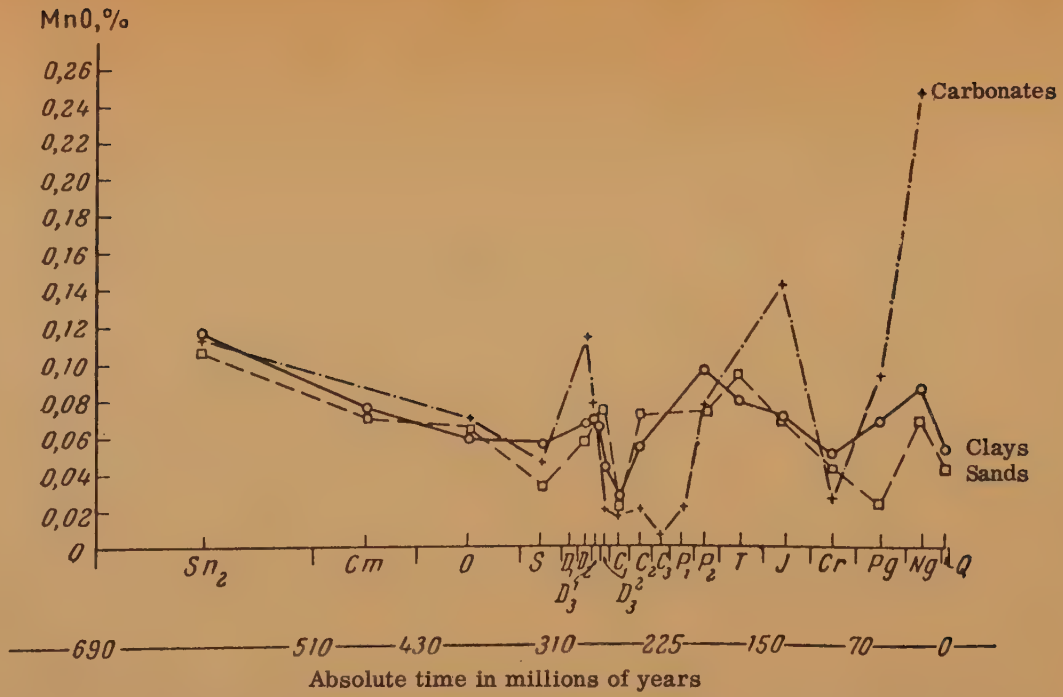

Fig. 2. Variation in MnO content is sands and silts, clays, and carbonate rocks of the Russian platform (sands and silts according to the data from 410 analyses of mean test samples prepared from 6361 specimens; clays according to the data from 404 analyses of mean test samples prepared from 8883 specimens; carbonates according to the data from 293 analyses of mean test samples prepared from 10389 specimens.

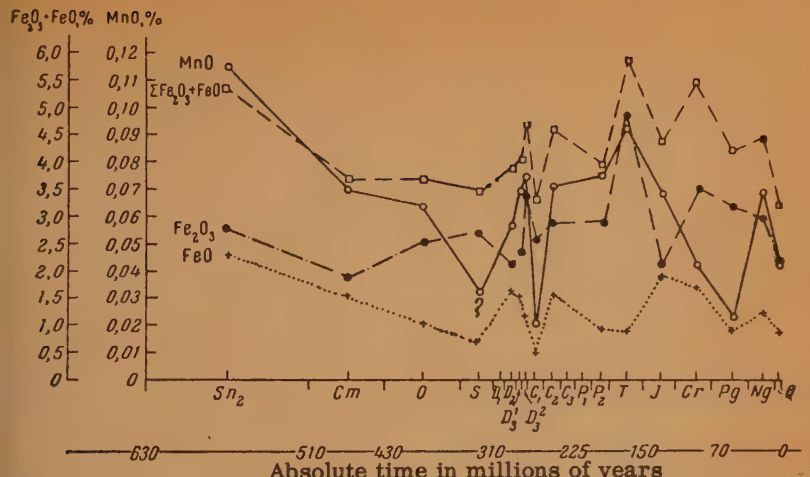

Fig. 3. Variation in the MnO, magnetite (Fe_2O_3 + FeO), Fe_2O_3 and FeO content in sands and siltstones of the Russian platform (according to the data from 410 analyses of mean test samples prepared from 6361 specimens)

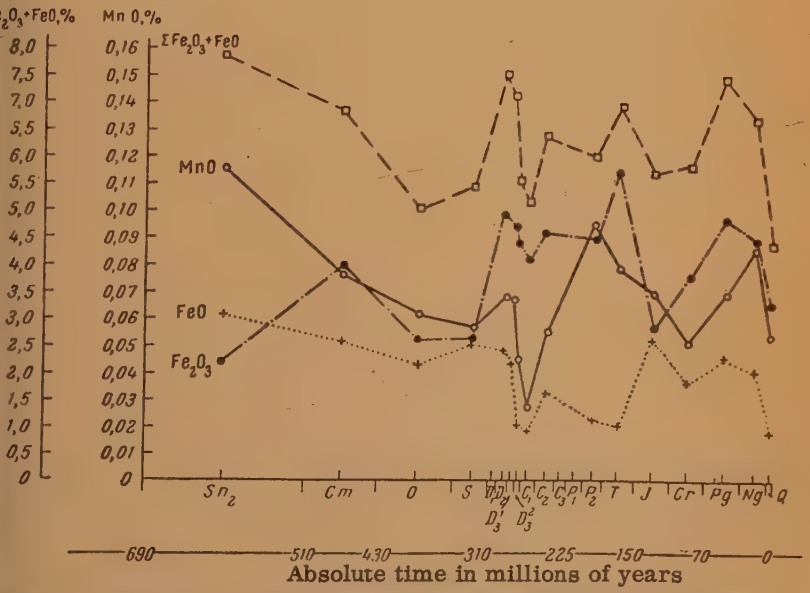

Fig. 4. Variation in the MnO, magnetite (Fe_2O_3 + FeO), Fe_2O_3 and FeO content in clays of the Russian platform (according to the data from 404 analyses of mean test samples prepared from 8883 specimens)

Note: Comma represents decimal point.

is parallel to the ferrous iron curve. Only in the epoch when there was a wide dissemination of red-colored rocks (D_3, P_2 and T) does the manganese curve deviate from being parallel to the FeO curve and follow the Fe_2O_3 curve instead. Manganese follows ferrous oxide closely in carbonate rocks (Fig. 5).

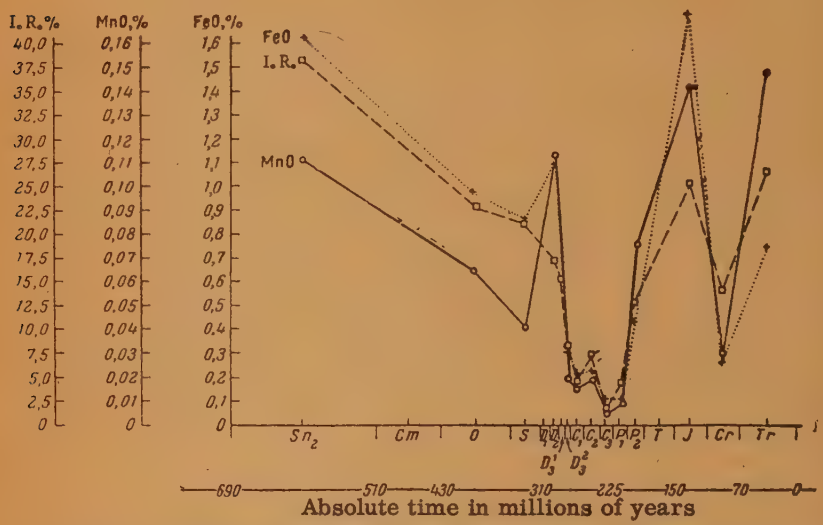

Fig. 5. Variation in the MnO, FeO and insoluble residue (I. R.) content in carbonate rocks of the Russian platform (according to the data from 293 analyses of mean test samples prepared from 10389 specimens)

Note: Comma represents decimal point.

The data under consideration leave no doubt that manganese in sedimentary rocks is paragenetically related to iron just as in magmatic rocks [8, 16, 27]. The ratio of manganese to iron remains approximately unchanged in the sands and clays. This is evident from the figures that follow below, and which were calculated for magmatic rocks from data due to A. P. Vinogradov [11]. The mean value of the ratio $\frac{MnO}{FeO + Fe_2O_3}$ is equal to 0.011 for ultrabasic rocks, 0.021 for basic rocks, 0.024 for neutral rocks and is 0.015 in acidic magmatic rocks, while this ratio equals 0.016 in sands and silts, and 0.011 in clays. Only in the carbonate rocks does a certain change in this ratio towards more manganese (0.040) begin to show, indicating that in zones of carbonate sediment accumulation there take place regional geochemical processes which lead to some separation of manganese and iron.

Processes which go considerably further in separating these two metals and lead ultimately to the formation of sedimentary manganese deposits develop locally and proceed only for definite values of the parameters pH and Eh for the erosion and sedimentation medium. In accordance with the

latest summary of K. B. Krauskopf [20] and a number of earlier papers, the separation of iron and manganese and the concentration of the latter occurs under the influence of various factors, among which essential roles are played by the lower solubility of the trivalent and bivalent iron compounds (for certain values of pH and Eh), the activity of iron and manganese bacteria, and the loss of acid solutions of manganese into an alkaline medium such as usually are ocean waters, subsurface waters of arid regions and contacts with limestones. In all cases it is supposed on theoretical grounds that the precipitation of manganese should be preceded by the sedimentation of considerably larger amounts of iron. This condition is far from always being true, and there are world-famous manganese deposits (Chiatura, for example) in whose vicinity it has not been possible to establish the presence of large accumulations of iron. On the whole, Oligocene deposits in the USSR and adjoining countries contain a number of sedimentary manganese deposits both large and small, while at the same time there are no iron deposits in them. Such correlations are one of the stumbling blocks of the modern theory of the process of manganese ore formation [20].

The physico-chemical conditions in the weathered layer and the intensity of the decomposition of continental rocks (predominantly basic rocks) are determined to a large extent by the climate. The most favorable is a humid and warm (subtropical) climate under which conditions there is a vigorous development of vegetation and there arises a surplus of organic acids which intensifies the decomposition of the rocks and creates a medium which is favorable for washing out various chemical elements, among them iron and manganese, from the weathered layers. Acidic waters carry them out in huge quantities into sea basins. The proximity of the majority of sedimentary manganese deposits to the coastal portions of ancient seas [1, 5, 6, 7, 17, 22, 41] makes it possible to surmise that the unloading of manganese from acid solutions took place in the contact zone between continental waters and the physico-chemically different alkaline medium of the sea. Just the same, elementary calculations show that altogether only thousandths of the total amount of manganese carried out from a continent are concentrated in ore bodies. Consequently, to solve the problem as to where the bulk of the manganese is precipitated, it is necessary to make the facies profile of this element more precise.

3. THE DISTRIBUTION OF MANGANESE IN ROCKS ACCORDING TO THE FACIES CONDITIONS OF THEIR FORMATION

We attempted to bring to light certain very general tendencies in the distribution of manganese by using statistical methods which had been developed earlier by one of the authors [29]. All the mean test samples of sands, clays and carbonates that were being studied were classified according to the facies conditions of formation of their constituent rocks into three principal types of deposits: 1) continental and lagoon, 2) sea coast, and 3) open sea (pelagic) deposits. In classifying the test samples as one facies type or another, we followed the data from the "Atlas of Lithological and Facies Maps of the Russian Platform" [3], introducing necessary corrections in accordance with more recent publications. In the case of interstratification of different facies types of deposits, the membership of the test sample in a given type was determined by the predominance of the number of layers of this type.

The results of the statistical computations for the mean manganese content of rocks of every type are given in Table 3, whose data are used in constructing the distribution curves for manganese (Figs. 6 and 7). From consideration of the curves in Fig. 6 it is evident that the maximum manganese content in all the types of rocks studied is associated with coastal facies

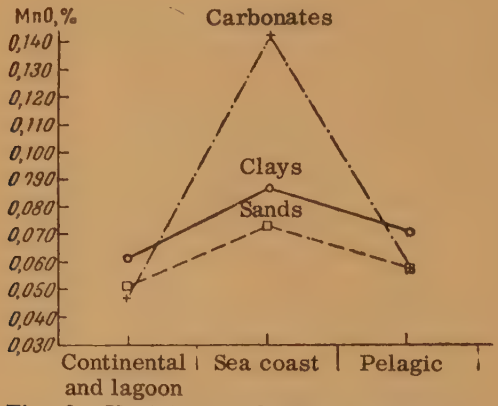

Fig. 6. Variation in the MnO content in sedimentary rocks according to the facies conditions of their formation (sands and siltstones according to the data from 410 analyses of mean test samples prepared from 6361 specimens; clays according to the data from 404 analyses of mean test samples prepared from 8883 specimens; carbonate rocks according to the data from 293 analyses of mean test samples prepared from 10389 specimens)

Note: Comma represents decimal point.

deposits. The amount of manganese in the rocks decreases from the coastal zone both in the direction of the continent towards the continental and lagoon facies deposits and in the direction towards the open sea to the pelagic facies deposits. Such in general outline is the distribution arrangement for sedimentary manganese deposits. The greater part of them is concentrated in deposits in the coastal areas of ancient seas. Their number in continental and lagoon facies deposits is relatively small. As for the pelagic portions of sea basins, sedimentary manganese deposits are completely absent here [5, 6, 7, 42]. There is an undoubted resemblance between the facies distributions of the manganese clarkes and the manganese ore concentrations which are natural consequences of different aspects of the same natural process: the migration of acidic manganese solutions from erosion areas into alkaline media in sedimentation basins. The formation of sedimentary manganese deposits proceeded against a background

of increased manganese clarke concentrations, and not the contrary, as is supposed by N. M. Strakhov [36].

Although the fact that the maximum accumulations of manganese are in coastal deposits is inherent for deposits of both the humid and arid climate zones, examination of the curves in Fig. 7 shows that climatic conditions

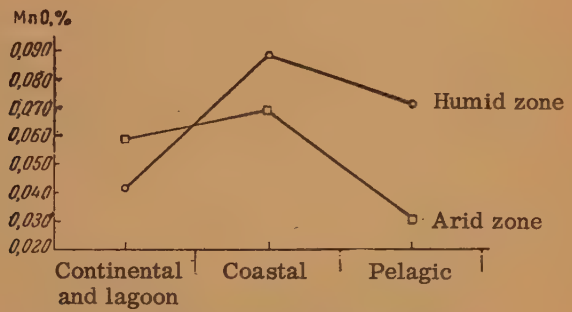

Fig. 7. Variation in the MnO content in Russian platform deposits according to the facies and climatic conditions of their sedimentation (according to data from Table 3)

Note: Comma represents decimal point.

have a considerable influence on the facies profile. Coastal deposits of the humid zone are richer in manganese than the deposits of similar facies in the arid zone. While the amount of manganese decreases in the direction of the continent towards the continental and lagoon facies, this occurs more rapidly in humid zone deposits than in arid zone deposits. The amount of manganese also declines in the direction towards the open sea, but in this case the drop in the manganese content occurs more rapidly in arid zone deposits. The differences noted were determined by the different intensity of the physico-chemical processes under different climatic conditions. The migration of manganese in acidic solutions which were rich in organic acids, such solutions being peculiar to a humid climate [2], travelled a greater distance and lasted for a longer time. Large amounts of migrating bivalent manganese, which had been extracted as a result of a thorough decomposition of continental rocks and which was almost completely unoxidized, were carried away from the erosion zones to beyond the limits of the acid medium of the continental facies where they had been detained slightly. They separated out as sediment as soon as they encountered the alkaline conditions of the sea. However, the powerful continental current freshened the waters of the sea basin to a great distance from the shore, creating a gradual gradient from acidic to alkaline values of the pH. As a consequence, this separating out of the manganese as sediment did not occur all at once, but was extended to a great distance from the shore, gradually diminishing beyond the limits of the zone in which the water was freshened.

But the migration of manganese proceeded differently under arid climate

conditions. The slight development of a vegetable cover limited the entry of organic acids into surface waters, and the latter's reaction was of a weakly alkaline or neutral character. The erosion of continental rocks which were located at their place of origin developed slowly and penetrated only to a small depth. Oxidation of bivalent manganese and the conversion of a large part of it into immobile forms of higher valence took place here. As a consequence of this, the total amount of Mn drawn out by surface and ground waters was much smaller than under humid climate conditions. The intensity of the continental current also was lowered as a consequence of the fact that the watershed was situated within waterless regions or those which were drought-afflicted and scanty in water. The migration routes for the Mn and their duration were considerably shortened. A considerable part of the manganese was captured by the alkaline media of the continental soils and sediments and stopped migrating for a long time as a consequence of the formation of immobile tetravalent compounds. The remaining part of the manganese was carried out to sea but was precipitated out as sediment in the coastal zone since the zone in which the sea waters were freshened was minimal under these conditions. Only an insignificant part of the original manganese reached the open sea in one form or another.

4. DISTRIBUTION OF MANGANESE IN THE AREA OF A SEDIMENTATION BASIN

The application of statistical methods enabled us to compensate for the varied and changing from epoch to epoch pictures of the distribution of manganese in different types of sedimentary rocks of the Russian platform and bring to light certain general regularities of this distribution in relation to facies and climatic conditions. However, important details of the actual distribution in the area of a given real sedimentation basin remained secret because of the limitations of the statistical method. This arrangement we attempted to chart by constructing quantitative lithologico-geochemical maps.

We constructed maps of the Givet and Frasnian stages and a number of graphs of the distribution of manganese in layers, of which only several maps, which depict the distribution of manganese in sand and silt (Fig. 8), clay (Fig. 9) and carbonate deposits (Fig. 10) of the Frasnian stage, are given here.

Frasnian sediments accumulated under the conditions of a humid and warm climate which began to change gradually only at the end of the Frasnian age and became more and more arid [28]. Frequent variations in the routine of oscillatory movements of the basin's bottom and the adjoining dry land (Baltic shield and Voronezh massif) had repeated shifts of the shore lines, the substitution of regressions for transgressions and periodic decreases and increases in the delivery of fragmental products into the basin as consequences throughout the course of the Frasnian age. All this determined the complexity of the map of the lighologico-facies conditions in the basin's area and the vagueness of the boundaries of the facies zones [28]. These complicated interrelations are depicted schematically by the lithologico-facies backgrounds of our maps, but they are given more completely and more systematically in a series of four maps published in the "Atlas of Lithological and Facies Maps of the Russian Platform" [3].

Comparison of the Frasnian maps with one another (Figs. 8, 9 and 10) reveals principally that the regions of distribution of positive and negative

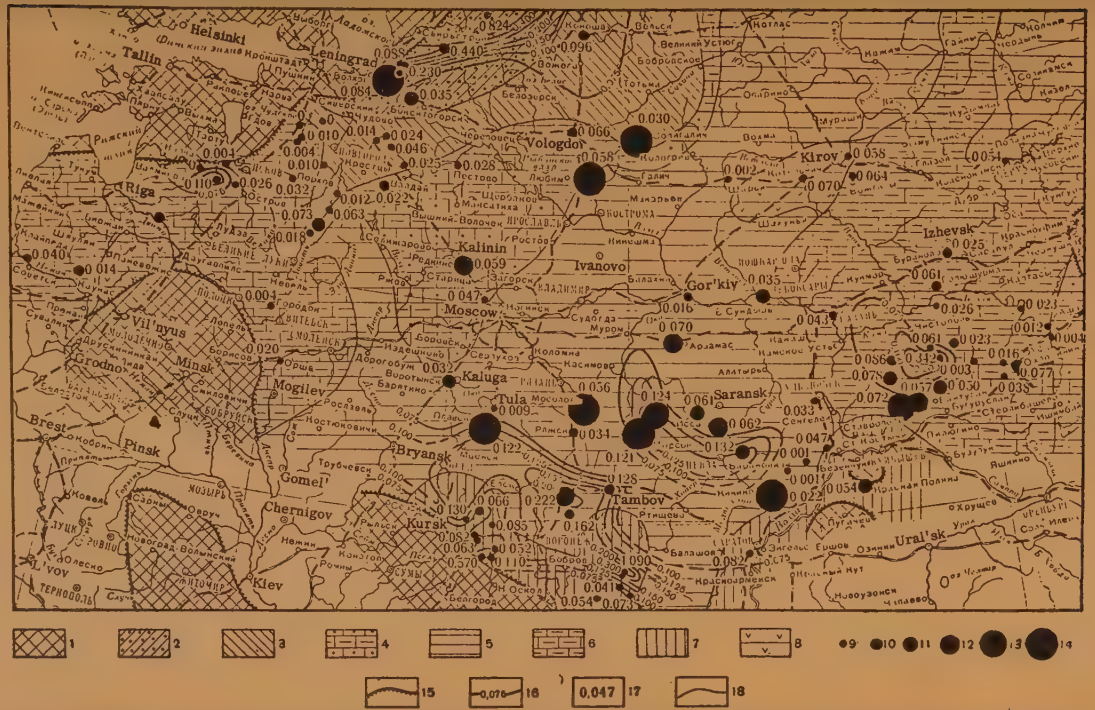

Fig. 8. Lithologico-geochemical map of the distribution of disperse MnO in sands andsiltstones of the Frasnian stage of the upper Devonian of the Russian platform (clays and sands of the lower Shchigry stage are present almost everywhere and are not included in the lithologico-facies background of the map). The map is drawn in accordance with the data from 104 analyses of mean test samples prepared from 1193 specimens.

Meaning of symbols: 1 - erosion regions; 2 - red-colored sands and clays; 3 - carbonate and clay rocks in the lower part of the cross-section; red-colored sands and clays in the upper part; 4 - carbonate rocks with clusters of marls, clays and sands; 5 - carbonate rocks with clay interlayers; 6 - carbonate rocks with subsidiary interlayers of marls and clays in the upper part of the cross-section; 7 - carbonate and clay rocks with sand interlayers; 8 - gypsums; 9 - mean test samples prepared from less than 10 specimens; 10 - mean test samples prepared from 10 to 20 specimens; 11 - mean test samples prepared from 20 to 30 specimens; 12 - mean test samples prepared from 30 to 40 specimens; 13 - mean test samples prepared from 40 to 50 specimens; 14 - mean test samples prepared from more than 50 specimens; 15 - boundary of an erosion region; 16 - line of equal MnO content in %; 17 - mean MnO content in a cross-section in %; 18 - boundaries between lithologico-facies zones.

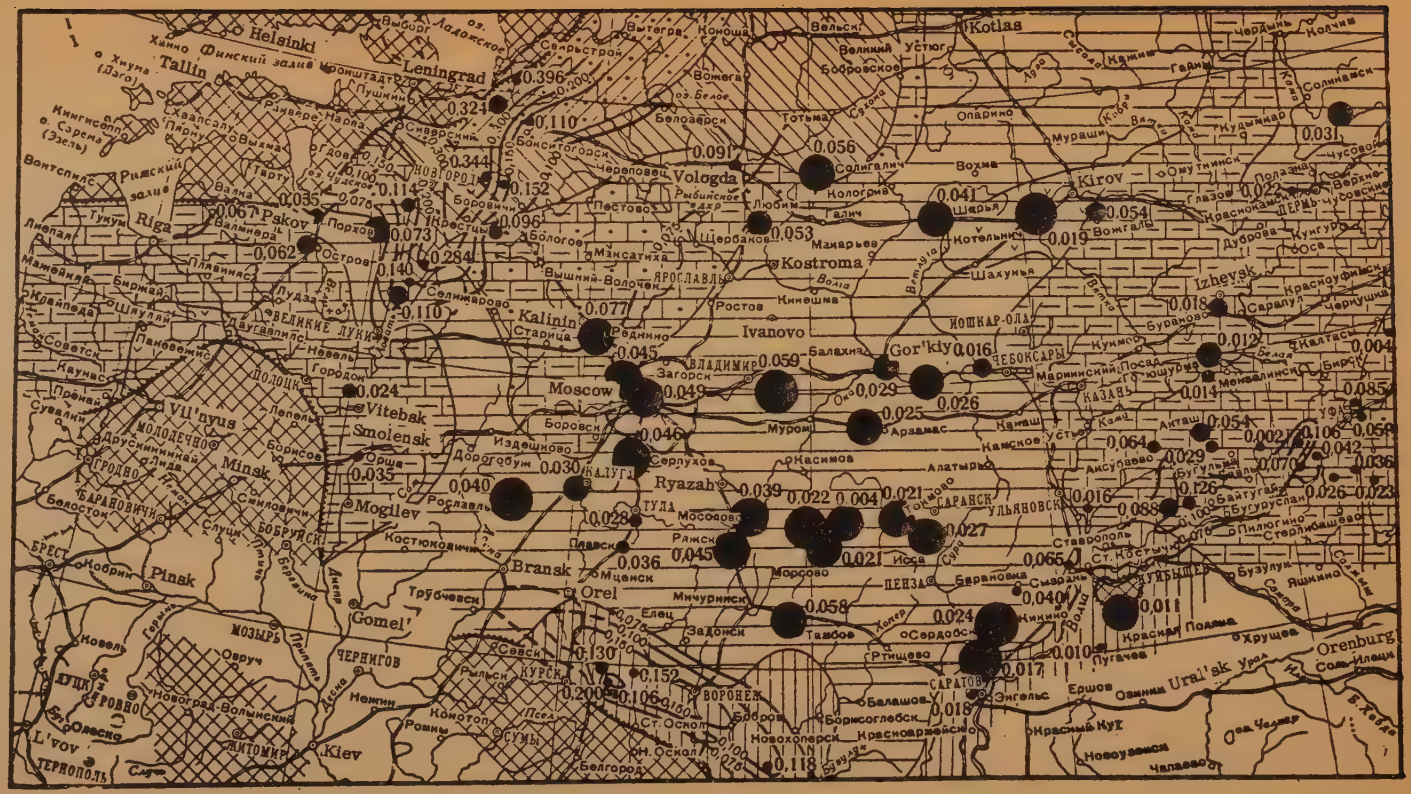

Fig. 9. Lithologico-geochemical map of the distribution of disperse MnO in clays of the Frasnian stage of the upper Devonian of the Russian platform (the conditional symbols are the same as in Fig. 8). The map is drawn in accordance with the data from 97 analyses of mean test samples prepared from 2012 specimens.

Fig. 10. Lithologico-geochemical map of the distribution of disperse MnO in carbonate rocks of the Frasnian stage of the upper Devonian of the Russian platform (the conditional symbols are the same as in Fig. 8). The map is drawn in accordance with the data from 84 analyses of mean test samples prepared from 2768 specimens.

manganese concentration clarkes in the basin area have similar outlines in rock deposits which differ in lithological content. The distribution regions of positive clarkes occupy only 6 to 8% of the sedimentation basin area being studied. Negative manganese concentration clarkes are principally correlated to the zone's pelagic zone. The largest regions of positive anomalies are drawn towards the coastal zones of those dry land areas which experienced upheavals and underwent erosion in the given time (Voronezh and Karelia dry lands). Small positive anomalies are associated with dips in interior tectonic upheavals (Tokmak and Tatar anticlines and the Vyatka bank), within whose limits were formed small but numerous islands, some of which rose above the level of the sea while others sank below. Positive anomalies did not form in the adjoining portions of the basin wherever the dry land was tectonically quiet and was situated within the limits of an arid and waterless climate zone (for example, the dry land surrounding the saline Baltic lagoon and the eastern slope of the Byelorussian massif). Negative manganese content clarkes developed here just as in the pelagic portions of a basin.

Differences in the degree of upheaval of the dry land and in the climatic conditions existing within its borders, as well as in the facies and hydrochemical conditions in the adjoining areas of the sedimentation basin, determined the location of the regions of positive manganese concentration clarkes.

In the event that the upheaval of the dry land was slow, while the climate was warm and humid, as was the case for the Voronezh dry land [28], the region of positive manganese concentration clarkes was pushed back by the fresh water current for some distance into the interior of the basin. A narrow strip of negative manganese concentration clarkes appeared immediately offshore in the zone where there was the greatest amount of freshening of sea waters. Characteristically, and this is precisely the situation here as was shown by the lithologico-geochemical maps for iron that we drew, there is a zone of positive iron concentration clarkes which is further from the shore. Within the limits of the latter, to the extent that there was an increase in the salinity of the waters and an increase in the pH, the manganese content in the sediments increased gradually, and upon reaching its maximum value, decreased again in the direction towards the open sea. In periods when there was an increase in the intensity of the upheavals, these periods being dated by the appearance of a zone of sandy streaks, and in consequence when there was an increase in the volume of the continental current, there was an increase in the breadth of the zone in which the water was freshened. As a result, all the negative and positive manganese concentration clarke zones which had been noted above increased in size and shifted in the direction of the open sea (Fig. 8). On the other hand, in the periods when there was a weakening of the upheavals and a decrease in the volume of the continental current, which correspond to the times for the formation of carbonate sediments, the breadth of the zone in which the water was freshened grew smaller, and all the zones which have been mentioned grew narrower and shifted towards the shore (Fig. 10).

It is not improbable that a certain role in the formation of regions of positive Mn and Fe concentration clarkes near the Voronezh dry land was played by the wide distribution of iron ore formations among the Precambrian rocks that were still at their place of origin in the Voronezh massif.

Somewhat different interrelations are established near the Karelia dry land which experienced more intense upheavals during the Frasnian age

than did the Voronezh massif. Immediately adjoining the erosion region there was a region in which sand and clay continental red-colored facies were dispersed, and within whose limits coastal carbonate accumulations wedged themselves in at times. Judging by the nearness of the Baltic salt lagoon, and by the polymictic mineralogical content of the sand bodies, the climate in this part of the Russian platform was more arid than in the more southern regions. The processes of chemical decomposition of rocks proceeded with less intensity on the Karelia dry land. The migration routes of the manganese became shorter. The bulk of the manganese was captured by sand and clay continental sediments and soils. In this way can be explained the fact that the zone of maximum manganese concentrations is contiguous to the Karelia erosion region. The amount of manganese in sandy and clay sediments diminishes gradually in proportion to the distance into the interior of the basin, with the zone of positive manganese concentration clarkes being comparatively narrow (Figs. 8 and 9). During periods of transgression by the sea, which correspond to the times for the formation of accumulations of limestones, the climate grew somewhat milder, the amount of atmospheric sediments increased, and river flow grew stronger. The oncoming sea washed out the manganese which had been fixed in the erosion crusts, soils and continental sediments [21], while a stream of fresh water from the continent pushed the manganese sedimentation zone back into the interior of the sea basin. As a consequence of this, the breadth of the region over which positive manganese concentration clarkes were distributed increased sharply (Fig. 10).

CONCLUSIONS

In summing up this investigation we are justified, on the basis of the data considered above, in drawing the following conclusions:

1. The manganese content in platform sediments varied periodically with the passage of geological time. As a rule, epochs of enrichment of sedimentary deposits with disperse manganese which correspond to the initial and final periods of the Caledonian, Hercynian and Alpine sedimentation cycles were synchronous with manganese metallogenic epochs. The formation of sedimentary manganese ore deposits proceeded under conditions of a general enrichment of coeval sediments with disperse manganese.

2. The bulk of the manganese dispersed in sedimentary rocks is paragenetically related to iron. The size of the manganese to iron ratio in sedimentary rocks is close to that in magmatic rocks. Some change in this ratio in favor of manganese is noted in carbonate rocks. The processes of separating these two metals, which ultimately lead to the formation of manganese deposits, become apparent locally and occur for definite values of the physico-chemical parameters (pH and Eh) of the erosion and sedimentation medium.

3. Maximal manganese content is associated with coastal facies deposits. The amount of manganese in the rocks gradually diminishes from the coastal zone in the direction of the continent towards the continental and lagoon facies deposits and more sharply in the direction of the open sea twoards the pelagic facies deposits. Such on the whole is the distribution scheme for sedimentary manganese deposits, the majority of which are concentrated in deposits in the coastal parts of ancient seas, while a small number is found in continental deposits and there is a complete absence from deposits

in the open sea. The beginning of manganese deposits was not an isolated phenomenon cut off from the general redistribution of manganese in the sedimentation process, and proceeded against a background of higher manganese concentration clarkes, and not the opposite, as is supposed by N. M. Strakhov.

4. The distribution of manganese in the areas of platform sedimentation basins is determined by a complex of climatic and tectonic conditions on the surrounding dry land. On the type of climatic conditions and the routine of tectonic movements depend the intensity of the erosion processes acting on continental rocks, the amount of manganese extracted and the mobility of its compounds, the physico-chemical conditions in the transporting medium and the places where the increased concentrations of manganese are deposited in sediments. Under the conditions of a humid climate the increased manganese contents in the sediments shift in the direction of the open sea, while under the conditions of an arid climate, on the contrary, the zone of maximum manganese concentrations migrates in the direction of the continent. An additional powerful factor intervenes in the distribution of manganese in geosynclines, namely, volcanism [43].

5. The regularities that have been revealed have a practical significance and should be taken into account in carrying out geochemical searches for manganese ores in platform sediment accumulation basins.

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THE AVERAGE COMPOSITION OF THE IGNEOUS ROCKS OF ARMENIA

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The paper discusses: 1) the average chemical composition of the principal types of extrusive and intrusive rocks, 2) the average composition of the main magmatic groups of igneous rocks, and 3) the general average composition of the igneous complex of Armenia. The average compositions of the principal types in each facies (intrusive and extrusive) were computed from the average compositions of the igneous rocks belonging to the same group and facies but differing in age, the relative abundance of each type being taken into account. The average compositions of the magmatic groups were computed from the average compositions of the different types belonging to each group. In computing these averages, the quantitative data on the distribution of the rocks were taken into consideration as far as possible, including both areal distribution and average thicknesses for the extrusives.

In the author's opinion, the characteristics of the average chemical composition of Armenian rocks hold for the Lesser Caucasus as a whole. The data used in the computations include analyses of rocks from Armenia and from the adjacent regions of the Lesser Caucasus, and it is precisely in these territories that the main part of the igneous rocks of the Lesser Caucasus is concentrated. To exhibit the chemical characteristics of Armenian igenous rocks, they were compared with Daly's average compositions and with the average compositions of similar complexes in other parts of the USSR.

The average compositions of the principal intrusive rocks of Armenia in terms of oxides and according to Zavaritzkii's numerical characteristics or parameters are given in Tables 1 and 2 respectively. When compared with Daly's averages, the average compositions of the principal intrusive rocks of Armenia reveal a number of peculiarities. The ultrabasic rocks are near Daly's amphibole peridotites and differ from them only in having higher MgO content, larger parameters b and s, lower content of SiO_2, Al_2O_3, FeO and $(Na_2O + K_2O)$ and larger parameter a. The gabbros differ from Daly's gabbros in containing more Al_2O_3 and CaO, having a larger parameter c, being poorer in SiO_2, FeO, MgO, Na_2O, $(Na_2O + K_2O)$ and having smaller parameters a, s, n and c'.

Table 1

Average Composition of the Principal Types of Intrusive Rocks of Armenia (%)

Rock type	Number of analyses	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	misc.	H_2O
Ultrabasic	26	39,57	—	2,66	4,90	3,10	0,10	34,38	4,68	0,15	0,07	9,71	0,62
Gabbroid	75	46,57	0,46	20,78	3,78	4,94	0,09	6,49	13,23	1,40	0.87	1,78	0,33
Quartz diorites	23	61,51	0,41	17,56	2,79	3,76	0,09	2,51	5,43	3,08	1,86	0,88	0,24
Granodiorites	21	64,33	0,56	16,55	2,68	2,55	0,14	1,01	4,19	3,20	2,86	0,72	0,51
Granites	26	67,66	0,36	15,61	1,42	1,64	0,09	2,03	2,91	3,57	4,52	0,86	0,17
Plagiogranites	20	72,01	0,28	14,77	2,05	1,46	0,06	1,34	2,40	3,98	0,88	0,93	0,33
Syenites	31	58,78	0,26	19,14	3,14	1,85	0,15	1,25	3,73	4,60	5,28	0,64	0,27
Nepheline syenites	29	56,72	0,23	21,78	2,68	1,26	0,12	0,62	2,56	5,31	6,51	1,57	0,43

Note: Comma represents decimal point.

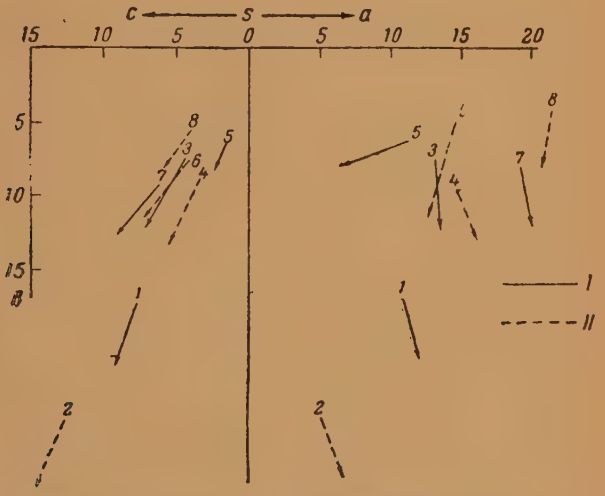
Table 2

Average Composition of the Principal Types of Intrusive Rocks of Armenia in Terms of Zavaritskii's Numerical Characteristics

Rock type	a	c	b	s	a′	f′	m′	c′	n
Ultrabasic	0,35	1,35	59,67	38,63	—	10,22	83,79	5,99	100
Gabbroid	4,84	12,50	25,16	57,50	—	34,20	47,20	18,60	69,69
Quartz diorites	9,79	6,71	11,50	72,00	8,54	53,66	37,80	—	71,44
Granodiorites	11,64	5,25	7,44	75,67	9,43	66,98	23,59	—	62,65
Granites	14,26	3,16	6,46	76,12	—	42,70	52,10	5,20	54,71
Plagiogranites	10,07	2,89	9 00	78 04	40,30	35,82	23,88	—	86,60
Syenites	18,50	4,05	7,54	69,91	—	62,26	29,24	8,50	56,92
Nepheline syenites	22,04	3,29	6,87	67,80	29,17	55,20	15,63	—	55,20

Note: Comma represents decimal point.

The quartz diorites are very near Daly's average type, but have higher Al_2O_3 content and slightly higher values of c and f' and a lower value of m'. The granodiorites are also similar to Daly's granodiorites but have higher Fe_2O_3 content and larger f' parameter with smaller n and m'. The plagioclase granites have a higher SiO_2 content than Daly's granites, larger parameters n and a', lower content of K_2O and $(Na_2O + K_2O)$ and lower values of a, f' and m'. The granites are characterized by a higher content of Al_2O_3 and CaO, higher values of b and m', lower content of SiO_2 and lower values of s, f' and n as compared with Daly's granite. The syenites and nepheline syenites differ from Daly's averages in having more Al_2O_3, larger c, less Na_2O and smaller a and n. The syenites are poorer in silica and have a smaller parameter s. The nepheline syenites, however, are richer in SiO_2 and have a larger value of s than Daly's type rock.



Average composition of rocks of both facies belonging to the same magmatic group

I – extrusives; II – intrusives

If tenths of one percent are considered, then the majority of Armenian intrusive rocks have more Al_2O_3 and larger c but less SiO_2, Na_2O and $(Na_2O + K_2O)$ and smaller a and n as compared with Daly's average compositions. For instance, all but the ultrabasic rocks are richer in Al_2O_3 and have a larger parameter c than the corresponding rocks listed by Daly. The ultrabasic rocks, gabbros, granites, syenites and granodiorites have less SiO_2 than the average rocks and the ultrabasic rocks, gabbros, syenites, nepheline syenites and quartz diorites have less Na_2O. Apart from granites, all other intrusive rocks differ from the average types by lower values of a and gabbros, granodiorites, granites, syenites and nepheline syenites by a lower value of n.

Table 3

Average Composition of the Principal Types of Extrusive Rocks of Armenia (%)

Rock name	Number of analyses	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	misc.	H_2O
Basalts and diabases	35	49,87	0,85	18,08	5,17	4,72	0,06	4,60	8,10	3,41	1,23	2,42	0,56
Porphyrites	55	52,30	0,70	17,51	4,33	4,94	0,10	4,43	7,14	3,17	1,21	3,65	0,48
Basaltic andesites	26	55,45	1,08	17,71	3,18	3,87	0,08	4,14	6,97	3,90	2,54	0,61	0,51
Andesites	44	60,37	0,67	16,92	3,37	2,58	0,08	3,01	5,12	3,85	2,25	1,43	0,33
Andesitic dacites	19	62,25	0,78	16,03	2,88	2,78	0,13	1,93	4,06	4,06	3,82	0,97	0,35
Tuffs	81	62,49	0,74	17,06	2,88	1,37	0,11	1,47	3,56	3,98	3,43	2,02	0,44
Dacites	35	64,97	0,32	15,91	2,74	1,14	0,03	1,24	3,43	3,84	3,10	2,42	0,71
Rhyolites	12	72,63	0,21	14,16	1,17	0,37	0,08	0,44	1,19	3,63	4,05	1,37	0,55
Quartz plagio-porphyries	16	73,05	0,27	12,13	2,67	1,13	0,44	0,92	2,06	4,04	0,81	1,79	0,36
Obsidians	12	74,82	0,06	13,34	1,23	0,26	0,08	0,13	1,07	4,28	4,12	0,44	0,10
Quartz porphyries	3	75,44	0,17	13,49	1,43	0,68	—	0,14	0,53	3,17	3,36	0,98	0,81
Trachyandesites	6	52,02	0,43	21,88	3,69	2,22	0,12	2,13	6,09	4,29	4,68	2,42	0,12
Leucite trachyte	5	55,37	0,38	21,57	2,35	1,83	0,18	0,86	3,90	4,30	6,87	1,93	0,41

Table 4

Average Composition of Intrusive and Extrusive Rocks of Armenia Belonging to the Same Group (%)

Composition	Facies	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	misc.	H_2O
Mafic	Extrusive	52,77	0,73	18,17	4,33	4,20	0,09	4,18	7,15	3,37	1,95	1,95	0,34
	Intrusive	46,57	0,46	20,78	3,78	4,94	0,09	6,49	13,23	1,40	0,87	1,78	0,33
	Extrusive	62,63	0,57	16,37	3,41	1,78	0,08	1,88	3,87	3,60	3,36	1,91	0,46
Intermediate	Intrusive	63,54	0,43	16,39	2,40	2,49	0,13	2,21	4,21	3,46	3,39	1,17	0,20
	Extrusive	73,46	0,22	13,21	2,16	0,80	0,11	0,60	1,25	3,74	2,34	1,61	0,45
Silicic	Intrusive	67,60	0,35	15,66	1,46	1,63	0,08	2,02	2,94	3,59	4,43	0,84	0,16
	Extrusive	53,69	0,40	21,72	3,02	2,02	0,15	1,43	4,99	4,29	5,77	2,17	0,26
Alkalic	Intrusive	57,40	0,23	20,91	2,70	1,43	0,12	0,86	2,97	5,38	5,80	1,40	0,53

Note: Comma represents decimal point.

The average composition of the principal Armenian extrusives is presented in Table 3. Comparing these rocks with Daly's averages, we find both resemblances and differences. It should be noted that these differences are better revealed by Zavaritskii's numerical characteristics (especially by the auxiliary ones) than by comparison of analyses.

The majority of the extrusive rocks of Armenia have lower TiO_2 and $(Fe_2O_3 + FeO)$ content than Daly's average rocks.

Table 4 gives the average compositions of the extrusive rocks of Armenia and of their intrusive equivalents. The data of Table 4 were used in constructing the appended diagram of average compositions of extrusive and intrusive rocks belonging to the same type. The vectors on the diagram are numbered in the same sequence as the average compositions in Table 4. The table and the diagram show that the average compositions of the extrusives and their intrusive equivalents belonging to the same group are very much alike if the content of the oxides is considered but differ considerably according to Zavaritskii's parameters. On both projections of the diagram and especially projection asb, the vectors of the intrusive rocks differ strongly from those of the extrusives in slope, length and position with respect to the coordinates.

Tables 5 and 6 present average chemical compositions of the principal types of Armenian igneous rocks. The average composition of basic rocks is near the composition of Daly's gabbros and basalts, differing from them only in a higher content of SiO_2, Al_2O_3 and $(Na_2O + K_2O)$. The intermediate igneous rocks occupy an approximately intermediate position between Daly's quartz diorites and granodiorites. The average composition of acid rocks is very near Daly's average for granite. The average composition of alkalic rocks is near the average composition of Daly's alkalic syenites, differing only in having a higher Al_2O_3 and CaO content.

A comparison of the percentage by weight of rock-forming elements in the principal types of Armenian igneous rocks, given in Table 6, with the average content of the same elements in the principal rock types of the earth's crust computed by A. P. Vinogradov [1] shows that Armenian rocks contain less iron and calcium. The silicic igneous rocks form an exception, for they are very near in this respect to the analogous rocks listed by Vinogradov. According to computations, the average composition of Armenian extrusives is near basaltic andesite; the average composition of the derivatives of silicic magma is intermediate between monzonites and granodiorites; and the average composition of intrusive bodies (including the rocks of the ophiolitic belt) is between diorite and quartz diorite.

Table 7 shows the average composition of Armenian igneous rocks. Of the total area of the igneous rocks of Armenia, extrusives occupy 92% and intrusives occupy 8%. However, the intrusives become much more extensive with depth, and the figures 80% for extrusives and 20% for intrusives were used in computing the average composition of the igneous rocks. The average composition computed on this basis is nearer actuality than the arithmetical mean of compositions or the average composition computed on the basis of areal distribution of the two facies. The average composition of Armenian igneous rocks is near the composition of diorites and basaltic andesites.

The average composition of Armenian rocks and the average compositions from other regions of the USSR are compared in Tables 8 to 11. The data for the other regions of the USSR were taken from S. P. Solov'ev [2]. Table 8 shows that the average composition of Armenian intrusives is more mafic than that of similar rocks from other regions of the USSR. It is

Table 5

Average Composition of the Main Magmatic Groups of Armenian Igenous Complex (%)

Magmatic groups	Number of analyses	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	misc.	H_2O
Ultrabasic	26	39,57	—	2,66	4,90	3,10	0,10	34,38	4,68	0,15	0,07	9,71	0,62
Mafic	200	52,65	0,72	18,22	4,32	4,21	0,09	4,23	7,27	3,33	1,93	1,94	0,34
Intermediate	351	63,31	0,46	16,38	2,65	2,31	0,12	2,13	4,13	3,49	3,38	1,35	0,26
Silicic	84	68,89	0,32	15,11	1,61	1,37	0,09	1,65	2,57	3,62	3,97	1,01	0,22
Alkalic	94	56,66	0,26	21,07	2,76	1,55	0,13	0,99	3,37	5,16	5,79	1,55	0,48

Table 6

Average Content of Petrogenic Elements in the Main Magmatic Groups of Armenian Igneous Complex (%)

Magmatic group	Si	Ti	Al	Fe^{2+}	Fe^{3+}	Mn	Mg	Ca	Na	K
Ultrabasic	18,20	—	1,38	3,43	2,69	0,07	20,62	3,32	0,11	0,05
Mafic	24,60	0,43	9,65	3,02	3,27	0,07	2,56	5,20	2,47	1,60
Intermediate	29,58	0,28	8,68	1,85	1,80	0,09	1,27	2,95	2,59	2,80
Silicic	32,18	0,19	8,00	1,13	1,06	0,07	1,00	1,84	2,68	3,30
Alkalic	26,47	0,16	11,16	1,93	1,20	0,10	0,61	2,41	3,83	4,81

Note: Comma represents decimal point.

Table 7

Average Composition of Armenian Igenous Rocks

Oxides	Content, wt. %	Elements	Content, wt. %	Zavaritskii's parameters	Value of parameter, wt. %
SiO_2	55,55	Si	25,95	a	11,66
TiO_2	0,60	Ti	0,36	c	6,50
Al_2O_3	17,39	Al	9,21	b	14,75
Fe_2O_3	3,97	Fe^{3+}	2,78	s	67,09
FeO	3,54	Fe^{2+}	2,75	a'	—
MnO	0,12	Mn	0,09	f'	47,8
MgO	3,45	Mg	2,09	m'	41,47
CaO	6,26	Ca	4,47	c'	10,73
Na_2O	3,37	Na	2,50	n	67,90
K_2O	2,45	K	2,03	—	—

Note: Comma represents decimal point.

nearest to the average composition of the intrusives of the Urals. In the intrusives of other regions, the SiO_2 content is from 7 to 12% higher than in the Armenian rocks. The latter, on the other hand, are richer in Al_2O_3, (Fe_2O_3 + FeO), MgO and CaO. The total alkali content of Armenian rocks is very similar to that of the rocks of the Caucasus but lower than in rocks of the other regions of the USSR. The rocks of the Urals are an exception to this statement, being poor in the alkalies.

As indicated by Table 9, the average composition of the extrusives of Armenia is similar to that of analogous rocks of the Caucasus, the Urals, Eastern Siberia and the Far East. With the exception of the Caucasus, Armenian extrusives have a somewhat higher Al_2O_3 content as compared with the rocks of these regions.

It follows from Table 10 that the average composition of Armenian extrusives, like that of Armenian intrusives, is somewhat more mafic than in the other regions of the USSR.

Table 11 presents the clarkes of the principal petrogenetic elements in the magmatic complexes of Armenia and of other regions of the USSR. An examination of this table reveals the following picture. The silicon content for the Armenian complex is considerably lower than for the other regions of the USSR. An especially high silicon clarke characterizes the rocks of Eastern Siberia and Middle Asia. The clarke of aluminum, on the other hand, is slightly higher for Armenian rocks than for the rocks of other regions. It is interesting to note that the clarke of sodium is more or less constant in the igneous rocks of the USSR, while the clarke of potassium varies within a rather broad range. The clarke of iron in the Armenian igneous complex is higher than elsewhere in the USSR. The igneous complex of the Urals is an exception, for the clarke of iron in it is approximately

Table 8

Average Composition of Intrusive Igneous Rocks from Different Regions of the USSR (wt. %)

	Armenia	Caucasus	Ukraine	North-western USSR	Urals	Middle Asia	Western Siberia	Eastern Siberia	Far East
SiO_2	53,83	67,03	68,69	69,47	59,04	69,63	68,53	71,18	69,07
TiO_2	0,49	0,46	0,43	0,45	0,13	0,33	0,39	0,33	0,40
Al_2O_3	16,48	15,14	14,71	14,69	12,61	14,70	14,39	14,38	15,78
Fe_2O_3	2,96	1,59	1,53	1,17	2,79	1,56	1,42	1,28	1,19
FeO	2,96	2,30	2,33	1,88	3,29	1,57	2,17	1,41	1,62
MnO	0,22	0,08	0,10	0,07	0,07	0,05	0,13	0,03	0,10
MgO	3,67	2,21	1,12	1,61	9,48	1,23	1,71	0,69	0,80
CaO	4,97	3,01	2,72	2,51	4,95	2,43	2,71	1,79	2,28
Na_2O	3,52	3,59	3,58	3,59	2,76	3,67	4,36	3,61	3,28
K_2O	2,94	2,88	3,83	3,60	2,37	3,28	3,23	4,29	4,46
H_2O	1,43	1,54	0,77	0,95	2,41	1,28	0,90	0,83	0,96

Note: Comma represents decimal point.

Table 9

Average Composition of Extrusive Rocks from Different Regions of the USSR (wt. %)

	Armenia	Caucasus	Ukraine	North-western USSR	Urals	Middle Asia	Western Siberia	Eastern Siberia	Far East
SiO_2	54,73	54,24	50,30	49,96	53,11	68,96	61,76	55,22	56,18
TiO_2	0,63	1,00	1,95	1,80	0,54	0,81	0,68	1,01	1,21
Al_2O_3	17,62	17,44	14,83	13,82	15,85	14,44	16,30	15,93	16,09
Fe_2O_3	4,22	3,95	4,54	4,17	4,18	2,35	2,59	4,31	3,68
FeO	3,68	3,34	7,87	9,00	5,86	1,91	3,97	4,80	3,82
MnO	0,09	0,14	0,23	0,27	0,05	0,15	0,16	0,17	0,16
MgO	3,39	4,11	4,96	6,18	4,75	0,63	2,08	4,21	3,91
CaO	6,53	8,04	7,69	7,92	9,23	1,41	4,39	6,57	6,09
Na_2O	3,33	3,36	3,18	3,05	3,36	3,21	3,50	3,07	3,39
K_2O	2,33	1,84	1,71	1,07	1,11	4,50	2,25	2,32	2,39
H_2O	2,49	2,32	2,42	2,65	1,75	1,44	2,19	2,18	2,61

Note: Comma represents decimal point.

Table 10

Average Composition of Igneous Rocks of Different Regions of the USSR (wt. %)

	Armenia	Caucasus	Ukraine	North-western USSR	Urals	Middle Asia	Western Siberia	Eastern Siberia	Far East
SiO_2	55,55	58,58	68,45	67,39	56,49	69,30	66,60	70,14	59,18
TiO_2	0,60	0,83	0,45	0,67	0,31	0,55	0,47	0,36	1,02
Al_2O_3	17,39	16,65	14,73	14,45	13,98	14,59	14,93	14,43	16,03
Fe_2O_3	3,97	3,15	1,57	1,49	3,40	1,93	1,76	1,47	3,11
FeO	3,54	2,99	2,40	2,68	4,37	1,74	2,68	1,66	3,31
MnO	0,12	0,12	0,10	0,09	0,05	0,11	0,14	0,05	0,15
MgO	3,45	3,45	1,16	2,06	7,46	0,95	1,81	0,92	3,19
CaO	6,26	6,32	2,79	2,91	6,78	1,98	3,18	2,11	5,22
Na_2O	3,37	3,43	3,57	3,78	3,03	3,45	4,12	3,56	3,36
K_2O	2,45	2,17	3,80	3,30	1,84	3,85	2,97	4,16	2,86
H_2O	2,28	2,10	0,79	1,15	2,13	1,36	1,25	0,91	2,22

Note: Comma represents decimal point.

Table 11

Average Content of Elements (Clarkes) in Igenous Rocks of Different Regions of the USSR (wt. %)

	Armenia	Caucasus	Ukraine	North-western USSR	Urals	Middle Asia	Western Siberia	Eastern Siberia	Far East
O	47,76	47,47	48,27	48,32	46,77	48,85	48,25	48,69	47,50
Si	25,95	27,34	31,94	31,45	26,39	32,34	31,08	32,73	27,62
Al	9,21	8,81	7,80	7,65	7,40	7,72	7,90	7,67	8,49
Fe	5,53	4,54	2,97	3,12	5,78	2,70	3,31	2,32	4,75
Mg	2,09	2,08	0,70	1,24	4,50	0,57	1,09	0,55	1,92
Ca	4,47	4,51	2,00	2,08	4,84	1,41	2,27	1,51	3,73
Na	2,50	2,54	2,65	2,80	2,25	2,56	3,06	2,64	2,49
K	2,03	1,80	3,15	2,73	1,53	3,20	2,47	3,45	2,37
Ti	0,36	0,50	0,27	0,40	0,19	0,33	0,28	0,22	0,61
Mn	0,09	0,09	0,08	0,07	0,04	0,09	0,11	0,04	0,12

Note: Comma represents decimal point.

the same as in the Armenian complex. The clarke of magnesium is similar and high in the igneous complexes of Armenia, Caucasus and the Far East. The clarke of calcium is similar and high in the complexes of Armenia, Caucasus and the Urals. A relatively high magnesium clarke is recorded from the igneous complex of the Far East.

The figures given in the first column of Table 11 indicate the average composition of the earth's crust in Armenia, for here sedimentary rocks are negligible as compared with igneous. Comparing the clarkes of the elements in Armenia with the clarkes of these elements in the crust, as computed by different investigators, we find that as a whole they are very similar. In general the clarkes of the elements in Armenia decrease in the same sequence as in the earth's crust. The clarke of magnesium, which is nearly equal to that of potassium, is the only exception.

Summary

Resemblances and differences have been found between the principal rock types of Armenia and Daly's average rocks. The differences between the average composition of Armenian igneous rocks and Daly's average rocks are more clearly revealed by Zavaritskii's numerical characteristics (especially auxiliary ones) than by analyses. In general, the average composition of the intrusives of Armenia is characterized by a higher Al_2O_3 content and lower SiO_2, Na_2O and ($Na_2O + K_2O$) content.

Most of the extrusive rocks of Armenia have lower content of TiO_2 and ($Fe_2O_3 + FeO$).

In general, the average composition of the intrusives differs from that of their extrusive equivalents by higher FeO, MgO and CaO content and lower Fe_2O_3 and Na_2O content. The average composition of Armenian intrusives is more silicic and alkalic than the average composition of the extrusives. The average composition of the igneous rocks of Armenia is near diorite and basaltic andesite. The average composition of Armenian intrusives is more mafic and often less alkalic than the average composition of analogous rocks from other regions of the USSR. The average composition of Armenian extrusives differs from that of the other regions of the USSR (except those of the Caucasus) in being richer in alumina.

The Armenian igneous rocks averages are more mafic than the average composition of other regions of igneous complex in the USSR. The igneous complex of Armenia is distinguished by a lower silicon clarke and often a lower potassium clarke, but it has a higher aluminum clarke and often higher iron, magnesium and calcium clarkes than the igneous complexes of the other regions of the USSR. The clarkes of some petrogenic elements in the igneous complex of Armenia are similar to those in the igneous complexes of the Caucasus, the Urals and the Far East.

In the igneous complexes of the USSR, the clarke of sodium is rather constant but the clarke of potassium is more or less variable.

The crust in the territory of Armenia has a somewhat higher Ca, Fe and Al and a lower Ti and K clarke than that of the earth's crust. The clarkes of the more abundant elements diminish in Armenia in the same sequence as in the earth's crust as a whole.

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THE SYSTEM WATER-CARBON DIOXIDE AT HIGH TEMPERATURES AND PRESSURES

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The knowledge of the solubility of carbon dioxide in water is very important for geology, since carbon dioxide is the second most important component of natural hydrothermal processes after water. However, the data in the literature relates principally to "room temperature" and only in two works [1, 2] goes up to a maximum of 100° and 120°C respectively. There are also data about the solubility of water in compressed carbon dioxide at 75°C and lower [3, 4]. In order to supplement this clearly insufficient data which geochemistry has today, we in the laboratory of magmatogenic processes under the direction of N. I. Kitarov undertook the study of the equilibrium relations in the system water-carbon dioxide up to temperatures of the order of 300°C and pressures of 600 kg/cm^2. Brief information about part of this work was published earlier [11].

In general, the phase equlibria in the binary systems of the gas-liquid type have been studied with sufficient care over a whole series of systems, eg. nitrogen-water, hydrogen-water, nitrogen-ammonia, nitrogen-sulfur dioxide, etc. They provide a basis for the analysis in a phase diagram of the water-carbon dioxide system.

1. INFLUENCE OF PRESSURE ON THE SOLUBILITY OF A GAS IN A LIQUID

In the simplest case, when [1] the solution of a gas in a liquid solvent is ideal, [2] the gas above the liquid behaves ideally (in the opposite case, the pressure must be replaced by the fugacity), and [3] the solvent is practically non-volatile, then the dependency of the solubility of the gas on the pressure is expressed by the formula:

$$\frac{d \ln N_g^l}{dp} = \frac{\overline{V}_g^g - \overline{V}_g^l}{RT} \qquad (I)$$

r in integrated form:

$$\ln \frac{p}{N_g^l} = \ln k' + \frac{\overline{V}_g^l p}{RT} \qquad (II)$$

here p is the total pressure of the system, equal to the pressure of the as; N_g^l is the mole fraction of the gas in the liquid solution; $\overline{V}_g^l$ is the par- al molar volume of the gas in solution, which is taken as independent of f the pressure; $\overline{V}_g^g$ is the molar volume of the gas in the gas phase; k' is enry's constant; R is the gas constant; T is the temperature in °K.

With increasing temperature the vapor pressure of the solvent becomes ppreciable (the solvent is volatile), besides, at pressures higher than ome atmospheres the pressure of the gas must be replaced by the fugacity, ence

$$\ln \frac{f_g^0 N_g^g}{N_g^l} = \ln k' + \frac{\overline{V}_g^l (p_1 - p_1^0)^*}{RT} \qquad (III)$$

here p_1^0 is the vapor pressure of the pure solvent; p_1 is the total pressure f the system; f_g^0 is the fugacity of the gas at the pressure p_1; N_g^g is the ole fraction of the gas in the gas phase; the remaining notations are the ame as in the previous equations.

From formula (I) it is obvious that, in general, the solubility of the gas ncreases as the pressure increases, $\overline{V}_g^g > \overline{V}_g^l$, however, at sufficiently igh pressures the relation shown can reverse itself, ie. $\overline{V}_g^l > \overline{V}_g^g$ and the olubility of the gas begins to decrease with pressure. The equality of $\overline{V}_g^l$ and $\overline{V}_g^g$ corresponds to the maximum on the solubility curve. Thus, the ourse of the solubility curve was experimentally found in the sulfur dioxide- itrogen system at pressures of the order of 5000 to 5500 kg/cm² [5, (see igure 1)] of the 25°C isotherm.

It is pertinent to emphasize that $\overline{V}_g^l$ is the apparent partial molar volume f the gas in solution. It is different from the true value and can be taken s equal to it (the true value - TR) only approximately. This is connected ith the insufficient strictness of the deduction of formula (III).

2. THE INFLUENCE OF TEMPERATURE ON THE SOLUBILITY OF A GAS IN A LIQUID

For the case of the slightly volatile solvent we have the relation

$$\left(\frac{\partial N_g^l}{\partial T}\right) = \frac{\overline{H}_g - H_g}{T\left(\frac{\partial \overline{Z}_g}{\partial N_g}\right)_{p,t}}$$

* (the equation of Krichevski-Kazarnovski)

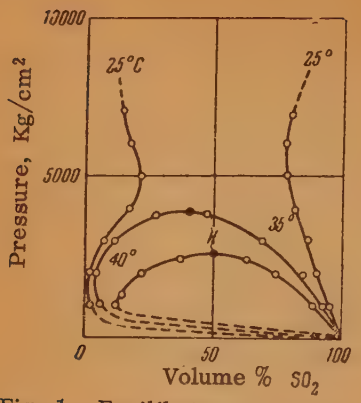

Fig. 1. Equilibrium relations in the system sulfur dioxide-nitrogen, according to the data of D. C. Tsiklis.

where N_g^l is the mole fraction of the gas in solution; $\bar{H}_g$ and H_g are the enthalpies of the gas respectively in solution and in the free state; $\bar{Z}_g$ is the partial molar isobaric potential of the gas in the solution.

In so far as $\frac{\partial Z_g}{\partial N_g}$ is always >O, the sign of the relationship is defined by the difference of the enthalpies $\bar{H}_g - H_g$, which in the physical sense represents the heat effect of the condensation of the gas to a liquid. The last quantity, as a rule, is negative since the solubility of the gas decreases with temperature. However, the above is not correct for every temperature: the heat effect of the condensation at sufficiently high temperatures can reverse the sign and this leads to a minimum in the isobars N_g-T. In figure 2 the isobars of solubility for the water-carbon dioxide system are presented according to the data of Wiebe and Gaddy [1]. From the figure it is clear that the pressure influences the location of the minimum.

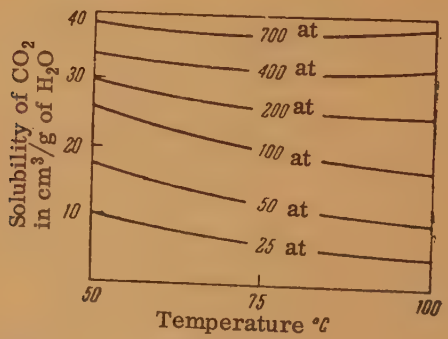

Fig. 2. Isobars of solubility of carbon dioxide in water after Wiebe and Gaddy.

3. THE SOLUBILITY OF THE VAPOR OF A LIQUID IN A COMPRESSED GAS

This dependency in the case of low solubility of gas in a liquid is expressed in the following form:

$$\frac{d \ln N_v^g}{dp} = \frac{V_l - \overline{V}_v^g}{RT}$$

where N_v^g is the mole fraction of the vapor of the liquid in the gas; V_l is the molar volume of the liquid; $\overline{V}_v^g$ is the partial molar volume of the vapor of the liquid in the gas.

Since, at low pressures, the derivative <0, the sign is negative, i.e., the solubility of the vapor in gas decreases with an increase of pressure. However, at greater heights of pressure, V_l can become greater than $\overline{V}_v^g$ and this leads to the appearance of a minimum.

In the water-carbon dioxide system, it appears at a pressure less than 100 kg/cm, at 50°C [3], which is connected with the very small value of the magnitude of $\overline{V}_v^g$ in consequence of strong electrostriction.

4. THE CRITICAL PHENOMENON IN THE GAS-LIQUID BINARY SYSTEM

As a result of the tendency of a gas and a liquid, forming a binary system, to mutually dissolve in one another, it is necessary to look for, at appropriate pressures and temperatures, a junction of both curves of solubility, accompanied by the critical phenomena.

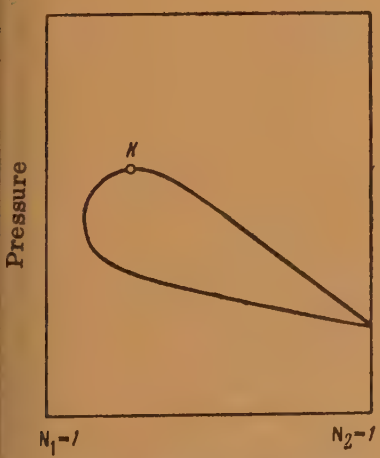

Fig. 3. Schematic diagram of the equilibrium of liquid gas in a binary system

In figure 3 is schematically represented a diagram of the mutual solubility in the coordinates P-N for the case, when the temperature of the system lies between the critical temperatures of the components, while the upper right branch is the liquid phase, the lower left is the gas phase and K is the critical point [6].

From the foregoing general considerations, it follows that the problem of studying the equilibrium relationships in the gas-liquid system, goes beyond a framework of simple change of the solubility of a gas in a liquid. As soon as we approach the critical temperature of the less volatile component there appears the necessity to consider the solubility of the gas in the steam of the liquid and to consider the critical phenomenon which represent the border cases of the mutual solubility of the components. All these considerations are relative in full measure to the system water-carbon dioxide at temperatures of 200 to 300° C and higher.

APPARATUS AND TECHNIQUE

The study of the solubility of carbon dioxide in water conducted by us on the apparatus,* the scheme which is shown in figure 4.

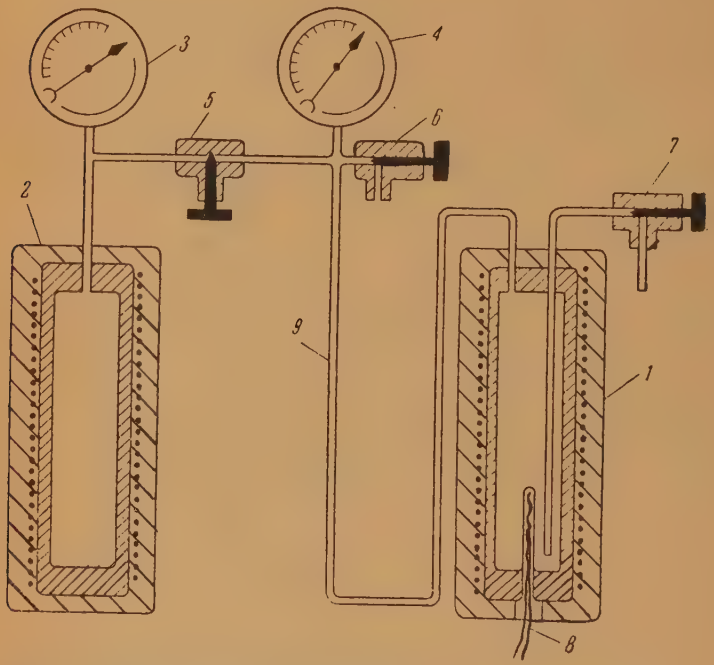

Fig. 4. Scheme of the arrangement for the study of the equilibrium relationships in the system H_2O–CO_2

1 – saturator; 2 – thermocompressor; 3 – manometer for the coarse measurement of pressure in the thermocompressor; 4 – manometer for the fine measurement of pressure in the saturator; 5 – by-pass valve; 6 – emergency valve; 7 – valve for sampling; 8 – measuring thermostat; 9 – flexible steel capillary

The so-called thermocompressor 2 was the source of carbon dioxide, i. e. autoclave by volume about 0.5l, filled with liquid carbon dioxide. By heating the thermocompressor, it was possible to attain a pressure of 600 atm. The filling of the thermocompressor was done from a carbon

*In the experimental work, T. I. Shekhanova took part.

dioxide cylinder, by means of freezing, for which the thermocompressor was cooled at the time of filling by solid carbon dioxide. During filling, the gas was allowed to pass across a dense felt filter for the purification from possible dirty oil. For the measurement of pressure in the system, a standard manometer 4 class 0.35 with a scale to 1000 kg/cm^2 was used. The saturation of water by carbon dioxide was done in a vessel of chrome-nickel steel, the so-called saturator, by insertion into a shaking stove 1. The saturator was connected to the manometer by a flexible steel capillary tube with an interior diameter less than 0.5 mm. In view of the significant volatility of the solvent (water) at temperatures above 200° C we had to forsake the dynamic method of saturation (as in the work of Wiebe and Gaddy (1)) and to use the static method.

For the mixing, a mechanical shaker was used, powered by an electromotor. The filling of the saturator with water was done through valve 7. For the removal of air, carbon dioxide was passed across the system before the beginning of the experiment. Since in all cases the attainment time of the equilibrium state remained unknown, the saturation was done by means of mixing at the predetermined pressure as well as by means of the preliminary supersaturation at higher pressure with a later lowering to the predetermined pressure. The reproduction of results obtained "from above" and "from below," served as a criteria of the equilibrium state of the system. For the sampling, the mixer was switched into the vertical position, thus the mouth of the sampling tube was shown to be in the liquid phase. Lowering of the pressure in the system in the process of sampling was continuously compensated by the giving out of carbon dioxide from the compressor with the help of the valve 5.

CONTROL OF TEMPERATURE AND PRESSURE

The thermo-regulation of the saturator was accomplished by a thermoregulator of the type. The temperature was measured by a millivoltmeter connected by chromel-alumel thermocouple 8. The thermocouple was graduated before the work and once during the work by the melting temperature of pure metals which allowed the temperature to be measured with an accuracy of ± 2°C. For the measurement of pressure a standard manometer of the class accuracy 0.35 was used. For the full verification of the measurement of the system a measurement of $p - t$ for water close to the critical temperature was conducted twice during the time of the work. The spread of the tabulated data [7] did not exceed ± 2 kg/cm^2, which under conditions of our work, lay within the boundaries of the error of measurement. The composition of the sample was determined by the weight method. For this purpose the water was collected in a special catcher (figure 5), in the process of the sampling, holding an acidified concentrated solution of sodium sulfate, and gas collected in a gas buret by volume about 400 ml under an acidified 20% solution of sodium sulfate, saturated previously with carbon dioxide. Upon completion of the sampling, the gas was directed by means of a three way tap into the potassium bulb where it is absorbed by the caustic alkalies. For the full catching of carbon dioxide, nitrogen was blown through the system, by preliminary drying and by purifying from carbon dioxide. For this the flow of nitrogen is directed through the system directly, avoiding the gas buret, by the same three way tap as above. Carbon dioxide and water are determined

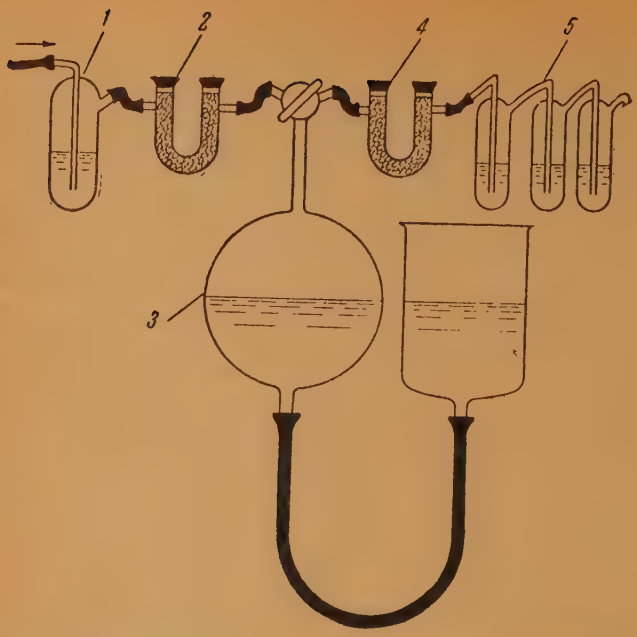

Fig. 5. Diagram of the apparatus for the analysis of samples of the liquid phase

1 - receiver of water (salt solution); 2 - U-shaped tube with anhydride for the catching of vapor; 3 - gas buret; 4 - U-shaped tube with calcium chloride for the drying of CO_2; 5 - capillary with 40% solution of KOH for the collecting of CO_2

by the increase of weight of the catcher. Together with the measurement of the solubility of carbon dioxide in the liquid phase of water, a series of measurements of the composition of the equilibrium gas phase of the system was conducted. For this the saturator was brought into such a position that the mouth of the sample tube was shown in the gas phase. Upon analysis of the gas phase, the quantity of gas in the sample was determined by the volume method, for which the gas buret was used, placed in a thermostat analogous to that which was used for the analysis of the samples of the liquid phase, but in larger volume (about 1150 ml). The quantity of gas in the buret was computed by tables with a correction for temperature, atmospheric pressure and pressure of the steam above the salt solution. The quantity of water in the sample was determined by the weight method as in the first case; also the composition of a series of samples of the liquid phase, taken at temperatures of 330°C, were determined by weight method. Since under the conditions of increased temperature in the presence of carbon dioxide, corrosion of the materials from the wall of the saturator was possible, some qualitative determinations of iron in the samples were done. Analyses showed the absence of iron.

EVALUATION OF RESULTS

The results obtained of the composition of the liquid phases are presented in Table 1A and graphically in figure 6. On this same graph are represented the isotherms according to Wiebe and Gaddy [1], recalculated in milligrams of dissolved carbon dioxide in one milliliter of water at room temperature. In Table 1B the compositions of the equilibrium vapor phases are presented and in figure 7 the full phase diagram of the system water-carbon dioxide in the coordinates pressure-composition, according to our data and the data in the literature. A comparison of these diagrams with the diagrams of the system sulfur dioxide-nitrogen according to the data D. S. Tsiklis (5 (figure 1)) reveals their general character. As is obvious from the figures, these diagrams are quite similar. In both cases we have to deal with the system liquid-gas, changing into a super critical state at the attainment of corresponding magnitudes of temperature and pressure, while the pressure lowers the temperature of the critical transformation of the system. In both cases by measurements of the increase of the temperature, there is an obvious tendency to "loop," to tie up to the axis $N_1 = 1$; at the boundary upon attainment of the critical temperature of the solvent, they are converted into a point. Consequently, for similar sorts of systems, the critical temperature of the less volatile components is the limiting temperature of the two phase state. For the system water-carbon dioxide, by analogy, it is pertinent to expect at known temperatures the appearance of maxima and minima in the curves of compositions of the liquid and gas phases respectively. For the verification of the reduced equation (III) above, determining the solubility of the gas in the liquid, we used the literature and our own data of the system water-carbon dioxide. In figure 8 the results of the comparison in the form of the isotherms in the coordinates

$$\log \frac{f^{\circ}_{CO_2} N^{g}_{CO_2}}{N^{l}_{CO_2}}$$

and $p - p^{\circ}$ are given. Besides, as is necessary from inspection of equation III, a linear dependence must take place. While the crossing of the lines with the ordinate gives the magnitude of the tangent of the corner slope of these lines with the abscissa gives the coefficient

$$\frac{\overline{V}_1}{2.303\,RT}.$$

Necessary values of the carbon dioxide fugacities for calculation were taken from tables, investigated in the work of Majumdar and Roy [8]. The 50° and 75° isotherms are constructed according to the data of Wiebe and Gaddy. The points lie satisfactorily on the lines. On the other hand, to encompass the isotherms 100° and 120° by straight lines was not possible. This is caused, apparently because the magnitude of $N^{g}_{CO_2}$ for the shown temperatures differs visibly from 1, and in our calculations, in view of the absence of data for this temperature, it is taken as equal to 1.

Our results also satisfactorily lie on straight lines except the 300° isotherm which is explained probably by the high mutual solubility of the components (consequently by the deviation of the solutions from the ideality) and the proximity of the critical region of the system where equation III is

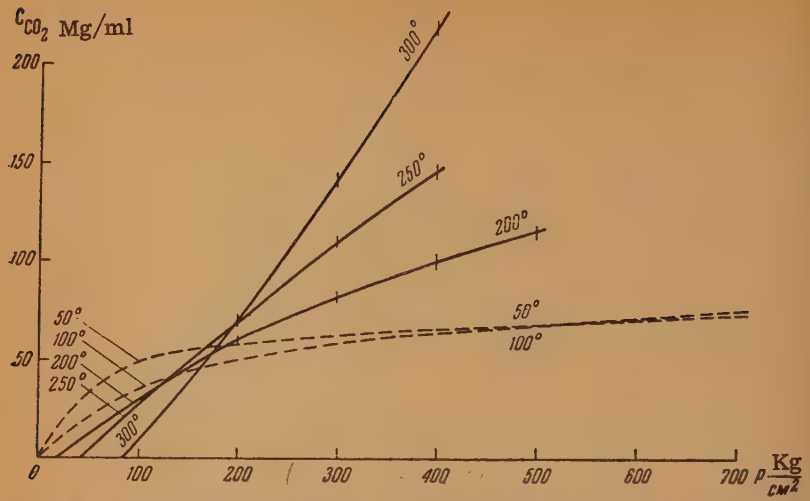

Fig. 6. The solubility of CO_2 in the liquid phase of water after Wiebe and Gaddy. The vertical lines show the scatter of results at the scale of the diagram

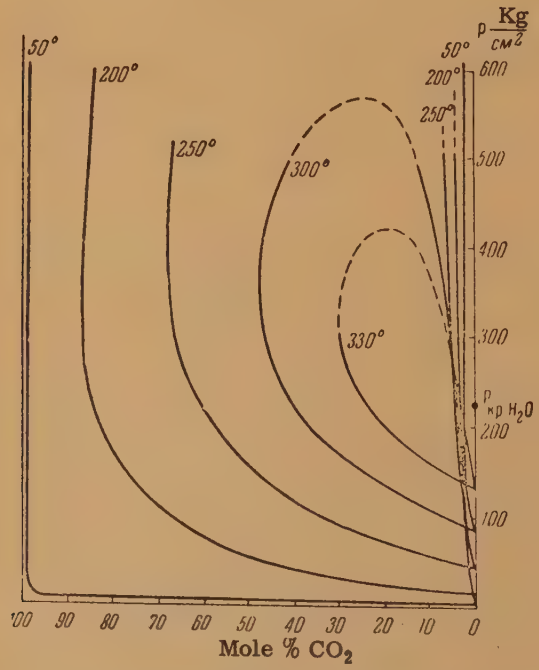

Fig. 7. General diagram of the system H_2O–CO_2

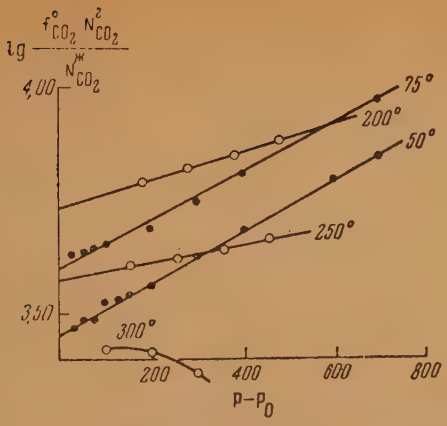

Fig. 8. Solubility of CO_2 in water under pressure. The lines are from equation III

not usable.

As is well known, in natural hydrothermal processes, not only pure water takes part, but water solutions of various salts in varying concentrations. Therefore, for the resolution of geochemical problems, connected with hydrothermal processes, systems of the type: water salt solution-carbon dioxide are especially interesting. However, the literature regarding these systems is even poorer than the literature concerning pure water. So for a temperature of 100 to 120°C we have only the data of Savage and Pratton [2]. These authors investigated the solubility of carbon dioxide in water solutions of calcium chloride with concentrations of 10.1, 20.2 and 30.2% admittedly up to the very significant pressures of carbon dioxide, i. e. 700 kg/cm^2.

In connection with this, a series of experiments were constructed by us, as an additional first step, for the study of solubility of carbon dioxide at higher temperatures corresponding to hydrothermal conditions. In order to have the opportunity of comparing our data with that of the literature [2], we used a solution with a concentration of 10.1%. Our choice was justified in that we put to the problem the institution of general regularities of the influence of the dissolved salts on the solubility of carbon dioxide, avoiding the complexities connected with the presence of many salts in the solution, as takes place in natural solutions. Further, in so far as calcium chloride possesses a positive temperature coefficient of solubility, we were guaranteed also from another possible cause of complication of the system — the precipitation of the solid phase at an increase of temperature. Finally for natural hydrothermal solutions, the concentration of salts of 10.1% in general is probably not quite so high and the data already obtained (so to speak) give a general picture of the phenomena. If we take only the last data on the character of the composition of solutions of liquid inclusions in iceland spar, they show the content of salts is from 47 to 231 g/l. [10].

For the work, we used the same apparatus and techniques as in the case of the system water-carbon dioxide. The study of the system salt solution-carbon

Table 1A

The solubility of CO_2 in H_2O

P kg/cm²	Concentration of CO_2 in mg/ml	Molar % CO_2
Isotherm 200°		
100	30,1*	1,22
	30,0	1,21
	30,2	1,22
200	61,9	2,47
	61,1*	2,44
	58,9*	2,35
	59,6	2,38
	60,2	2,40
	60,4	2,41
300	82,9*	3,28
	81,9	3,24
	80,2*	3,17
	83,4*	3,29
	82,5	3,26
	82,5	3,26
400	97,6	3,84
	100,0*	3,93
	101,8	4,00
	103,0*	4,05
	95,7*	3,76
	95,5	3,76
500	113,7*	4,44
	112,3	4,39
	116,8	4,56
	111,8*	4,36
	112,0	4,38
	114,0	4,56
	110,6*	4,36
	109,6	4,38
		4,45
		4,32
		4,28

P kg/cm²	Concentration of CO_2 in mg/ml	Molar % CO_2
Isotherm 250°		
100	26,5*	1,07
	26,4*	1,07
	26,7	1,08
200	69,6*	2,77
	69,0	2,74
	64,1	2,56
	68,8*	2,74
	68,1	2,71
	70,1	2,79
300	110,6*	4,34
	110,3	4,34
	106,2	4,17
	109,6	4,30
	112,1	4,40
400	147,1*	5,69
	145,1*	5,61
	143,1	5,53
	144,8*	5,60
	143,1*	5,53
	144,5	5,58
	143,4	5,54
500	169	6,5
	178	6,6
Isotherm 300°C		
160	43,9*	1,76
	45,2	1,81
	43,1*	1,73
200	71,6*	2,85
	69,7*	2,78
	68,9	2,74
	68,0	2,71
300	141,1*	5,45
	138,9	5,38
	144,9*	5,59
	141,6*	5,57

P kg/cm²	Concentration of CO_2 in mg/ml	P kg/cm²
Isotherm 300°		
500	137,3*	5,32
	139,2	5,40
	136,9	5,30
	141,8	5,49
400	213,9*	8,06
	223,4*	8,38
	221,3	8,31
	213,0*	8,03
	220,5	8,29
500	359	12,8
Isotherm 330°		
300	268	6,1
	260	5,9
	264	6,0

Note: The asterisks indicate data obtained as a result of saturation from above.

Comma represents decimal point.

Table 1B

The content of CO_2 in the vapor phase of the solution

P kg/cm²	Molar % CO_2	P kg/cm²	Molar % CO_2
Isotherm 200°C		Isotherm 300°C	
200	84,9 85,1 84,7 83,4 85,0 84,2	300	45,2 46,0 45,0 46,6 46,5
600	81,8	400	45,1 45,8 44,5 43,4 47,0
Isotherm 250°C			
200	64,4 63,0 65,6 61,5	500	40,3 41,1 41,3 41,0
500	67,3 67,4 66,9 69,4	Isotherm 330°C	
Isotherm 300°		300	26,5 29,0 28,7
200	38,2 36,7 37,0 36,0 35,9		

Note: Comma represents decimal point.

dioxide is connected with complementary difficulties of method and also of a technical order: firstly, during the sampling of the liquid phase there occurs a concentration of the solution in conjunction with the exit of part of the water from the solution into the steam phase, the concentration of salt in which is significantly less than in the liquid and this must especially strongly tell during the sampling of the vapor phase. Therefore, it was necessary to strive for a minimum quantity of the sampled liquid phase and completely give up the analysis of the vapor phase; secondly, the salt solutions at temperatures of 200 to 300° strongly corroded the material of the walls of the reactor, far stronger than pure water with carbon dioxide under the same conditions.

The results obtained are brought forth in table 2. In the graph, figure 9, the isotherms of solubility of carbon dioxide in 10.1% solution of calcium chloride according to our data and the data of Praton and Savage are shown in comparison with the isotherms of solubility for pure water, constructed according to our data and the data of Wiebe and Gaddy. The pairs of isotherms, representing equivalent temperatures, but relating to pure water and the salt solution are connected by an arrow for clarity.

All these data show that although the presence of dissolved salt lowers the solubility of carbon dioxide (the phenomenon of desalting) however, the general course of the isotherms remains the same

Table 2

The solubility of CO_2 in 10.1% solution $CaCl_2$

t°C	P kg/cm²	C_{CO_2} mg/ml
	100	16,3
	200	34,1
200	286	42,2
	400	53,3
250	200	33,8
	300	49,8
300	150	15,0
	250	38,8
	400	76,5
350	300	31,2

Note: Comma represents decimal point.

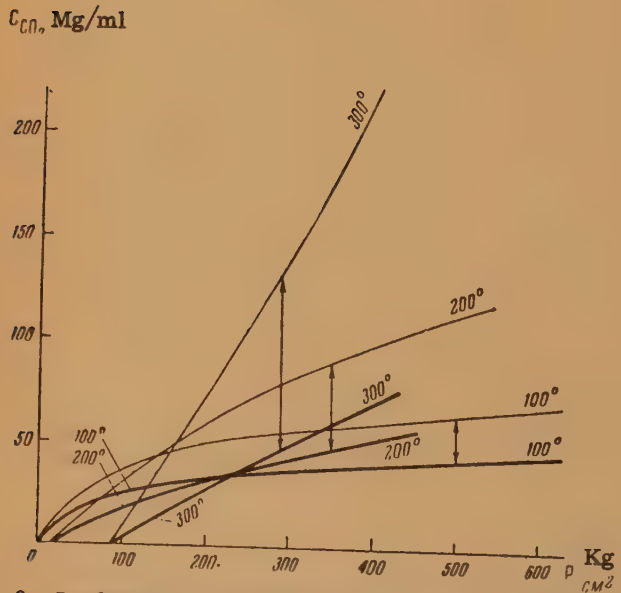

Fig. 9. Isotherms of solubility of CO_2 in H_2O and in 10.1% (1.83N) solution of $CaCl_2$. The narrow line relates to water, and the heavy line relates to the solution.

as in the case of pure water as well as in the case of the solution. Besides, the addition of 10% calcium chloride (by weight) decreases the solubility of CO_2 on the average by 1.5 — 2.5 times (depending on the temperature

and pressure). The form of the general diagrams of liquid-gas in both cases will also probably be similar, only critical phenomena will set in at higher temperatures, corresponding to the higher (critical) temperatures of salt solutions compared with pure water, and the branches of the curves, representing liquid-gas equilibrium, will be further displaced along the composition axis toward $N_{CO_2} = O$, as a result of the lower solubility of CO_2 in salt solutions compared with pure water. In the case of solutions of other compositions, the picture is certainly complicated: [1] by the possibility of mutual chemical reactions of carbon dioxide with the components of the solution and [2] by the possible precipitation of those salts, whose solubilities decrease with temperature (carbonate, sulfates, and others). In the case of the solution of calcium chloride the probability of precipitation of $CaCO_3$ is excluded, since in agreement with data of Chamberlain and Boyer [9] for the suppression of decomposition of calcium carbonate by hydrochloric acid requires a pressure of carbon dioxide of the order of 10^8 kg/cm^2.

The iron contained in the sample on account of the corrosion of the apparatus (up to 8g/1) must, evidently, somewhat distort the results on the side of the higher solubility of carbon dioxide (up to 6 mg/ml), inasmuch as carbon dioxide is also present in the form of iron carbonate in the solution.

CONCLUSIONS

1. The study of the solubility of carbon dioxide in the liquid phase of water in the region of temperatures from 200 to 300°C (in one separate case to 330°C) and pressures from 100 to 500 kg/cm^2 is in supplement to the data of the literature which is bounded at the temperature of 120°C.

2. According to the data of the compositions of the gaseous phase, in equilibrium with the liquid phase, a general diagram of the system water-carbon dioxide was constructed for temperatures from 50° to the critical temperatures.

3. Comparison with the diagram liquid-gas for the system sulfur dioxide-nitrogen according to the literature data discloses their similar character. In both cases, the pressure lowers the temperature of the critical transfer of the system and gives a basis to surmise by analogy the presence of a maximum on the curve of solubility of the gas carbon dioxide in the liquid phase of water and of the minimum in the curve of solubility of the vapor of water in the gas of carbon dioxide at corresponding temperatures.

4. It is shown that the equations of solubility of a gas in the liquid are applicable to the system water-carbon dioxide to 250°C.

5. In the example of 10% water solution of calcium chloride, part of the system was studied: the water salt solution-carbon dioxide in the ranges 100-400 kg/cm^2 and 200 to 300°C.

6. The solubility of carbon dioxide in 10% solution of calcium chloride is 1.5-2.5 times less than in pure water, however the general course of the curves of solubilities are similar in general characteristics.

7. In natural solutions, it is necessary to expect as great a variety in respect to the composition of the salts contained in them as in their concentrations, therefore, the question about the phase relationships in them is rather complicated and requires special descriptions in each separate case. As regards water with calcium chloride content in it of the order of

10% or less, then the solubility of carbon dioxide in it is acknowledged to be very significant.

8. The general considerations developed in relation to the diagram of water-carbon dioxide apparently are also valid to a certain extent for the systems with salt solutions.

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THE MODE OF OCCURRENCE OF URANIUM IN GRANITES

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The study of the mode of occurrence of different trace elements in rocks and minerals is one of the most important problems of geochemistry. In this connection the radioactive elements are of especial interest. This is due not only to their importance but also to the variety of techniques available for the investigation of their trace amounts.

In the present paper we shall discuss some of the problems arising in the investigation of the mode of occurrence of uranium in granites by the method of differential leaching.

Leaching tests provide indirect clues to the form in which a given element occurs in a rock or mineral.

The form of occurrence of an element is deduced from the results of differential leaching as described by I. E. Starik and his co-workers, who were the first to use this method [5, 6], or from the relative amount of the element dissolved under given conditions [3, 4, 9].

In recent years a number of papers have appeared in which it is concluded on the basis of leaching of a considerable fraction of uranium from rocks that "mobile," "free," "extra-silicate" and "non-diadochic" uranium forms play an important role in granites. But the terms defining the state of uranium themselves and the fact that large amounts of uranium are leached out under given conditions give certain arbitrariness to the interpretation of the phenomenon.

In some American experiments reported in part in the papers by E. S. Larsen, Jr., G. Phair and others [3, 4], uranium was leached out of rocks by boiling in acids. During this process, from 25 to 98% of the uranium content and from 2 to 30% of the minerals from which uranium was leached passed into solution. This is a rather drastic procedure, and it is quite clear that a number of minerals including such widespread uranium concentrators as apatite and allanite were completely or partially dissolved.

L. V. Tauson's experiments [9] were made under less rigorous but still aggressive conditions, by an hour's boiling of rock samples in a 5% solution of ammonium carbonate with addition of hydrogen peroxide. In these experiments also 10 to 96% of the uranium was leached out of different granites.

The leachable part of uranium was interpreted as the part occurring in minerals in non-diadochic form. It was supposed that this part may

consist of submicroscopic segregations of uranium minerals or of uranium dispersed as atoms or molecules. It was admitted that in altered rocks uranium may be present in secondary uranium minerals and in adsorbed state.

In a later work Tauson [8] interpreted the occurrence of rare elements in igneous rocks in non-diadochic form as a result of attainment of "diadochic saturation" by the concentrator minerals and the "ejection" of the remainder not admitted into the mineral lattices. The non-diadochic element was assumed to be present in the form of the simplest compounds, oxides or sulfides.

All these ideas are fruitful and pose a number of interesting questions relevant to our problem.

It has already been remarked that difficulties may arise in the interpretation of leaching experiments performed on rocks as a whole without observations on the behavior of individual minerals under the conditions of the experiment and without taking superimposed processes into account. For instance, since boiling in acids causes partial or complete solution of a number of minerals, not all of the extracted uranium can be assumed to have existed in the rock in the "free" state.

To get a better idea of the state of uranium leached out of granites in Tauson's experiments [9], we leached it out (under the same conditions) of certain minerals in which uranium is supposed to occur as a diadochic substitute (zircon, monazite, apatite).

It turned out that several tens percent of uranium may be leached out of these minerals.

A zircon (from the Il'men' Preserve) yielded 30% of its uranium by leaching (it contained 7.4×10^{-2}% U). An apatite (Panfilova Varaka) yielded 22% of its U by leaching (its U content was 5.3×10^{-3}%). But a monazite from Chkalov yielded only 3% of its U under the same conditions.

Thus, in two cases the percentage of leaching was comparable with leaching from granites, and this means that at least a considerable part of leached out uranium (extracted under given conditions) may be credited to the common accessory minerals or to their submicroscopic crystallites. The nature of uranium bonding in these minerals is not quite clear at present.

Such experimental procedure does not show clearly what particular minerals or uranium compounds contain leachable uranium in granites.

Evidently, if comparison is made of the results of leaching made under strictly identical conditions for different rocks and minerals, in which the form of occurrence of uranium is well known or is based on a well substantiated hypothesis ("mineral standards," so to speak) we shall be able to come closer to the solution of our problem. By gradually changing the conditions of the experiments it will be possible, very likely, to establish several forms of occurrence of uranium in rocks and minerals.

We shall report the results obtained by us in 1950 in leaching rocks and minerals with 0.2N solution of Na_2CO_3. The leaching was continued for five days with mechanical stirring of the sample, which caused considerable oxidation of uranium by atmospheric oxygen.

The ratio of the weight of the sample to the weight of the solution was 1:10. Under the conditions of the experiment, the rock-forming minerals were not dissolved but the part of uranium present in a relatively free state (oxides, secondary minerals and adsorbed compounds) was easily dissolved and remained in solution. Thus, unlike other investigators [3, 4, 9], we selected much "milder" conditions, under which only the easily soluble,

dispersed uranium was extracted.

The filtered soda solution (after leaching) was treated as follows. The filtrate was acidified with HCl to acid reaction and boiled to remove CO_2, a few drops of hydrogen peroxide being added to decompose organic matter. Then iron (2-3 mg of Fe as $FeCl_3$ solution) was introduced into the solution to act as a carrier for uranium, and the two metals were precipitated together with CO_2-free ammonium hydroxide. The precipitate was separated, dissolved in 15% HCl and evaporated, and uranium was extracted with 10 ml of 1N Na_2CO_3 solution.

The solution was centrifuged and its uranium content determined by fluorescence.

Let us examine the average values obtained in leaching uranium out of different rocks of the Tien Shan Range (Table 1).

The first group [1] contains granites unaltered or little altered by postmagmatic processes. As the table shows, the amount of uranium leached out of these rocks ranges from a few tenths to one percent. The visible uranium concentrators are the common accessory minerals, zircon, sphene, allanite, monazite and apatite.

The second group (II) includes the slightly greisenized granites (greisenization is muscovitization and partial silicification). Here the result of leaching is approximately the same as from the unaltered granites. The uranium-bearing accessory minerals are thorite, zircon and sphene.

The third group (III) includes granites altered by the relatively low temperature postmagmatic processes (fluoritization and chloritization). Here leaching was more intensive and amounted to several percent. The main accessory mineral is zircon, occurring in several generations.

The fourth group (IV) is composed of the granites from the Chernovinsk and Turgusun massifs (Altai) carrying accessory uranium titanate. In addition there are the usual accessory minerals, zircon, monazite and apatite. The percentage of leaching is comparable to that in the third group.

The fifth group (V) contains granites with uranium oxides and secondary uranium minerals. In this case the percentage of uranium leached out is much higher and amounts to several tens percent.

Similar experiments with certain sedimentary rocks show that the amount of leachable uranium in metasedimentary rocks is small, of the order of 0.1-3.0%; in unconsolidated rocks, 4 to 10%; but in the rocks containing uranium oxides or secondary uranium minerals it increases sharply to several tens per cent.

While the conditions of these experiments were simple and in nature the conditions are varied and complex, it is possible, nevertheless, to make certain qualitative deductions from the results.

It may be asserted that the substantial increase in the leachability of uranium (under the conditions of our experiments), both from granites and from sedimentary rocks, occurs when uranium is present largely in the form of oxides or of secondary minerals.

The slightly higher leachability of the postmagmatically altered granites and Altaian granites containing uranium titanate may be noted, but it is, after all, incomparably smaller than in granites containing uranium oxides and secondary uranium minerals.

These statements may raise a number of objections. The first factor to be taken into consideration is the degree of decomposition of the granites. It is possible that this factor largely determines the effectiveness of leaching. However, special leaching experiments (under the same conditions)

Table 1

Rock	U content in rock, n · 10^{-4}%	Percent of leached uranium	Range of variation	Number of samples
I. Slightly altered granites				
Porphyritic granite, Terskey Ala-Tau	3-7	0.8	0.3-1.4	8
Porphyritic granite, Kungey Ala-Tau	3-5	0.6	0.5-0.8	5
Porphyritic granite, Susamyr	4-6	0.3	0.2-0.4	2
Leucocratic granites, Terskey Ala-Tau	6-8	1.2	0.8-1.6	2
II. Greisenized granites				
Leucocratic granite, Sary-Bulak	6-7	1.0	0.7-1.5	3
Leucocratic granite, Sary-Mainak	15-18	1.3	0.4-1.8	5
III. Chloritized granites				
Leucocratic granites, Barskaun	7-8	2.7	2.2-3.2	2
Leucocratic granites, Dzhet-Oguza	10-12	2.5	0.8-3.5	8
IV. Granite with uranium titanate				
Biotite granite, Chernovinskii massif	14-16	3.2	1.8-4.1	3
Biotite granite, Turgusun massif	8-10	2.6	1.6-3.6	2
V. Granites with uranium oxides and secondary uranium minerals				
Pegmatoidal granite with uraninite	4.0	20	-	1
Granite with pitchblende	20-35	60	40-80	2
Granite with pitchblende	40-60	70	50-90	3
Granite with torbernite	200-470	85	70-90	4
Granite with schroeckingerite	155-250	90	80-100	2

Table 2

Degree of Leaching of Different Minerals

Minerals	Genesis	Uranium content in mineral, %	Degree of leaching, %
Brannerite	Hypothermal	37.0	0.2
Samarskite	Pegmatitic	10.4	0.1
Monazite	Pegmatitic	0.12	0.1
Monazite	Accessory (from placer)	0.25	0.003
Zircon	Pegmatitic	0.03	0.4
Cyrtolite	Pegmatitic	1.8	0.4
Allanite	Pegmatitic	0.15	1.0
Sphene	Accessory (from placer)	0.03	0.2
Fluorite	Hydrothermal	$1 \cdot 10^{-3}$	1.0
Muscovite	Pegmatitic	$4 \cdot 10^{-4}$	1.0
Quartz	Pegmatitic	$1.1 \cdot 10^{-4}$	1.0
Microcline	Pegmatitic	$3.5 \cdot 10^{-4}$	0.8
Magnetite	Skarn	$0.9 \cdot 10^{-4}$	6.0
Magnetite	Accessory (from placer)	$2.8 \cdot 10^{-4}$	2.0
Magnetite	Pegmatitic	$2.0 \cdot 10^{-3}$	10.0

made on several intensively decomposed granites show that the maximum leaching from common granites does not exceed 7%; i.e., it is much less than from granites containing supergene uranium minerals and uranium oxides [2].

Evidently a more direct answer to the question of the form of occurrence of leachable uranium in granites may be obtained by differential leaching of uranium from different minerals. To this end uranium was leached from the principal rock-forming and accessory minerals of granites.

We used mainly pegmatitic minerals and to some extent vein and accessory minerals of granites (panned from a placer).

Table 2 presents the results of these experiments. All minerals were leached under the same conditions as the rocks.

Table 3 gives the results of leaching of uranium from minerals of the same type but collected from uraninite-bearing pegmatites. Here the rock-forming minerals may be expected to contain dispersed uranium oxides or the products of their alteration.

The data on the leaching of secondary uranium minerals and uranium oxides are not given in the table, because under the conditions of our experiment they are soluble if sufficiently comminuted and treated with a large enough volume of solvents. This is known from our experiments and from a number of other investigations.

A number of conclusions may be drawn from an examination of the tables.

1. Monazite, zircon, sphene, fluorite and allanite yield a low percentage of uranium (hundredths, tenths parts of one percent, seldom 1%), and it is significant that placer minerals give lower figures (hundredths of one percent) probably because of the solution and abrasion of the surface films during prolonged transport.

2. The essential minerals of granites (taken in this case from pegma-

Table 3

Degree of Leaching of Minerals
from Uraninite-Bearing Pegmatites

Minerals	Uranium content in minerals, %	Degree of leaching, %
Monazite	0.5	0.4
Zircon	0.05	1.0
Quartz	$1.5 \cdot 10^{-4}$	35
Quartz	$0.7 \cdot 10^{-4}$	30
Microcline	$0.5 \cdot 10^{-4}$	100
Plagioclase	$7 \cdot 10^{-3}$	50
Plagioclase	$1.5 \cdot 10^{-4}$	20
Magnetite	$6 \cdot 10^{-4}$	15

tites), quartz and the feldspars differ in their behavior depending considerably on the type of pegmatite from which they are collected. If they are taken from pegmatites not carrying uraninite, the percentage of uranium leached out of them is low (as in common granites). If they are collected from a uraninite pegmatite, the percentage of leached out uranium increases and reaches several tens percent (this is true of minerals relatively rich in uranium and those poor in it). It should be noted that these samples do not contain microscopically detectable uraninite.

3. For the understanding of the form of occurrence of dispersed uranium, the leaching of magnetite is of special interest. It is improbable that uranium occurs diadochically in magnetite, but it must be present in it in the form of independent compounds. Very probably it is present as an oxide, and if so, according to the experiments, it should be easily leached out. Actually, uranium is leached from magnetite more easily than from many other minerals. But the degree of leachability varies for different magnetites. For example, magnetite taken from a zone which received a certain amount of uranium oxide is leached more easily because of the presence of uranium oxide coating on the faces of its crystals. On the whole, however, the percentage of leachable uranium in magnetites is too low for the uranium oxide alone to be responsible for their total uranium content.

There is a good reason for supposing, therefore, that when rocks or individual minerals under the conditions of our experiments possess high uranium leachability of about 10% or several tens percent, uranium is present in the form of secondary minerals and oxides. The leachable uranium in granites, amounting to tenths of a percent or a few percent of the total uranium, is completely accounted for by the presence of uranium in the finely dispersed accessory minerals (down to molecules) in which uranium is probably present as a diadochic element.

In order to make certain that the dissolved uranium represents the entire soluble fraction under given conditions, rather than the fraction corresponding to equilibrium under these conditions, it is necessary to make repeated leachings of the same material.

In all our experiments the second leaching was considerably less than the first, indicating that in all cases the bulk of uranium was extracted on

the first leaching.

At this stage of investigation, we can evidently make semi-quantitative separations of uranium present in granites in the form of oxides, secondary minerals or adsorbed compounds. These forms of occurrence of uranium are probably always secondary in granites and in granite-forming minerals [2, 7, 10]. Considering that uranium is very active chemically, it appears very improbable to us that these forms of uranium and uranium dispersed as atoms [1] could originate during the crystallization of magma.

Very probably, in the common granites, not altered by postmagmatic processes, uranium occurs in the finely dispersed accessory minerals. In this case, the distribution of the different forms of uranium among different accessory minerals (or their crystallites) and the manner in which it is bound in them may be qualitatively determined by the method of differential leaching under somewhat more rigorous conditions, so that the less mobile compounds are leached out.

In conclusion, we express our gratitude to I. E. Starik for valuable advice and help in this research.

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THE CHARACTERISTICS OF DISTRIBTION OF SOME RARE ELEMENENTS IN METAMORPHIC ROCKS, GRANITES, AND RARE METAL PEGMATITES OF THE SAYAN MOUNTAINS

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For a number of years the author has studied rare metal pegmatites of the Sayan Mountains and the enclosing schists and amphibolites intruded by different Upper Proterozoic granites.

The average mineralogical composition of the more typical rare metal pegmatites is approximately as follows:* quartz, 25-35%; microcline, 20-30%; albite, 10-20%; muscovite, 5-10%; and tourmaline, up to 3-5%.

In addition, the pegmatites contain: spodumene, beryl, muscovite, rose muscovite, rubellite, garnet, heterosite, sicklerite, purpurite, eucryptite, amblygonite, epidote, apatite, sphene, zircon, sericite, cassiterite, columbite, ilmenite, pyrite, chalcopyrite, magnetite, limonite, chlorite and a number of other minerals. Pyrrhotite, loellingite, biotite, holmquistite, and calcite occur at contacts with the enclosing rocks.

The distribution of the minerals in the pegmatites is not uniform. A number of pegmatite veins are characterized by alternation of blocky segregations of microcline with quartz-spodumene and albitized areas. In some veins the quartz-spodumene or microcline areas contain equidimensional or lenticular monomineralic segregations of translucent light-gray quartz (up to 3 m across). Locally the veins are enriched in tourmaline.

The microcline areas are most characteristic of only slightly albitized pegmatite dikes. They vary greatly in size. In the albitized pegmatites they are usually small and of very irregular shape (relicts).

In the slightly albitized veins the microcline areas may be several meters across. They are composed mainly of course, almost monomineralic segregations of gray microcline with subordinate amounts of quartz, spodumene, tourmaline, beryl, and other minerals.

The microcline areas, as has already been mentioned, alternate frequently with blocky segregations of quartz and spodumene. The quartz-spodumene areas are also variable in size. The largest segregations

*According to visual estimates at outcrops and in mine workings.

occur in the swells of thick pegmatite dikes. The distribution of spodumene in quartz is rather uniform. Occassionally, however, quartz-spodumene areas are observed in which the uniformly distributed spodumene of approximately uniform grain size (5-7 by 2-3 cm) is associated with two large (up to 1 m in length) spodumene crystals. Characteristically, the fine-grained spodumene is absent in these cases.

Spodumene, as a rule, is found in intimate association with light-gray quartz, which corrodes the faces of the spodumene crystals.

Occasionally, in some pegmatite veins, the masses of fine-grained gray quartz enclose small areas, up to 0.5 m across, composed of oriented crystals of spodumene measuring up to 3 x 0.5 cm.

The quartz-spodumene areas contain microcline, tourmaline, and a number of other minerals.

The albitized areas are dense fine-grained aggregates, often containing relicts of single crystals of quartz, spodumene, small crystals of later spodumene, and other minerals. In some veins these relicts constitute a large part of the total mass and in others they occur in subordinate amounts.

The peripheral zones are more intensively albitized than the central zones.

A detailed microscopic examination of the albitized zones reveals that the small albite laths are often oriented in the same direction and from peculiar sheaves or bundles. Individual albite laths are curved. In the areas of most intensive albitization there are thin chain-like veinlets of late quartz cutting the laths of albite. These areas also contain apatite, sphene, calcite, skeleton crystals of spodumene, and rather well-formed crystals of beryl. In the albitized zones spodumene is intensively replaced by sericite.

The albitized zones usually form wavy contacts with the microcline and quartz-spodumene segregations in the pegmatite bodies. In some veins, however, the boundaries between albitized and nonalbitized zones are rather sharp and relatively straight. Albite occurs also in late fractures in pegmatites and even forms veins of its own in the enclosing rocks.

In one case, in a thin pegmatite apophysa, areas rich in quartz-muscovite aggregate were found.

In some dikes, cleavelandite occurs in association with rubellite, rose muscovite, and other minerals.

An analysis of the paragenesis of minerals in the rare metal pegmatites showed that microcline crystallized first from the pegmatitic melt and formed blocks of varying size. Later than microcline are spodumene-quartz intergrowths in which spodumene is slightly earlier than quartz. Like microcline, spodumene and early quartz form blocky segregations. Approximately contemporaneous with early quartz are large crystals of black tourmaline, beryl, garnet, iron and manganese phosphates and a number of other minerals.

After the crystallization of these minerals the pegmatites were subjected to intensive sodium metasomatism (albitization) and the primary pegmatite minerals (mainly microcline and spodumene) were altered. Intimately associated with the intensive development of fine-grained albite was the crystallization of small needles of black tourmaline, of the second generations of spodumene and quartz and of some other minerals. The author believes that simultaneously with this there occurred a partial replacement of medium-grained beryl developed in quartz resulting in the formation of small beryl inclusions in albite.

On the basis of the distribution of material in a number of pegmatites, the author separated (according to the principal minerals) the following characteristic mineralogical complexes typical for the majority of veins: 1) microcline, 2) quartz-spodumene, 3) quartz-tourmaline, 4) quartz-muscovite and 5) albite.

During the investigation of pegmatites and the enclosing rocks, average samples weighing 6 to 10 kg were taken from quartz-mica schists and amphibolites (massive and schistose), from different types of granites (two-mica, biotite, and hornblende granites) from a number of pegmatites, from each of the pegmatitic mineralogical complexes and from biotite-bearing quartz-plagioclase dike rock which is younger than the pegmatites.

Analyses for lithium, rubidium, and cesium were made by flame photometry (by G. N. Popova, analyst of the Institute of Mineralogy, Geochemistry and Crystal Chemistry of Rare Elements) and for beryllium by spectrography (analyst N. N. Rodionov of the same institution). The analyses are presented in Table 1.

The table shows that lithium is present in both massive and schistose amphibolites in amounts ranging from 0.114 to 0.126%. It occurs in hornblende (0.163-0.388%), which in the schistose amphibolites contains 0.388% Li and in the massive amphibolites, 0.163% Li. The higher lithium content in the schistose amphibolites is explained by the fact that in addition to the common hornblende they contain holmquistite formed from pegmatitic solutions, possibly as a result of sodium metasomatism. During this process lithium was transferred from spodumene into the enclosing amphibolites, and the formation of holmquistite was the result. No cesium was found in the amphibolites.* The beryllium content amounts to 0.0002%. In granites, the lithium content increases from the two-mica granites (0.004%) to the biotite granites (0.1%). The rubidium content in granites increases in the same order from 0.015%-0.025% to 0.036%. No cesium was found in granites.* The BeO content in granites varies from 0.00026 to 0.0003%. According to the δ spectrographic analysis, beryllium is associated with hornblende and micas.

The contents of lithium, rubidium, cesium, sodium, and potassium vary greatly.

The content of lithium in different pegmatites ranges from 0.0127% (vein 19) to 0.638% (vein 24); of rubidium, from 0.038% (vein 19) to 0.150% (vein 23); of cesium, from 0.0033% (vein 24) to 0.019% (vein 23); of sodium, from 2.97% (vein 23) to 4.20% (vein 19); and of potassium, from 0.70% (vein 24) to 3.24% (vein 17).

In spite of this variation in the alkali content, the sum of the alkalies is approximately the same in all veins and amounts in each one to 6.5-5.5%; only in vein 11 does it rise to about 7.4%.

The K/Rb ratio in the pegmatites is 23; the K/Cs ratio is 204 (averaged from samples from nine veins).

The average beryllium content in the samples from nine pegmatites is 0.02%; it varies in individual dikes from 0.018% to 0.060% and depends entirely on the content of beryl.

The average content of K, Na, Rb, Cs, and Li and the ratios of these elements to each other in these schists, amphibolites, granites, pegmatites

*Average Cs content is less than 1 p.p.m.

Table 1

Content of Li, Rb, Cs, Na, K and Be, % * (average of two determinations)

Name of rock or mineral	Elements					
	Li	Rb	Cs	Na	K	Be
Shales	0,07	0,010	not found	1,04	1,63	—
Amphibolites (massive)	0,114	0,015	not found	1,53	0,55	0,0002
Amphibolites (schistose)	0,126	0,030	0,016	1,66	0,75	0,0003
Two-mica granite	0,004	0,025	not found	2,66	3,30	0,00026
Biotite granite	0,007	0,015	not found	2,45	2,49	0,00029
Hornblende granite	0,012	0,036	not found	2,30	2,23	0,0003
Pegmatites	0,320	0,103	0,0087	3,72	2,95	0,05
Dike rock with biotite	0,110	0,030	0,010	3,42	1,38	0,00035
Content in pegmatite veins **						
Vein 11	0,442	0,126	0,0085	3,92	4,13	0,026
" 12	0,0205	0,040	0,0054	3,93	2,53	0,031
" 17	0,1030	0,041	0,0076	3,25	3,24	0,023
" 18	0,060	0,053	0,0104	3,50	1,90	0,027
" 19	0,0127	0,0385	0,0045	4,20	1,26	0,06
" 21	0,2700	0,066	0,0120	3,78	1,55	0,048
" 22	0,210	0,107	0,0110	3,72	1,50	0,028
" 23	0,360	0,150	0,019	2,97	2,08	0,018
" 24	0,6280	0,099	0,0033	4,13	0,70	0,022
Content in the mineralogical complexes of a series of pegmatites						
Microcline	0,039	0,342	0,015	—	—	0,0021
Quartz-spodumene	1,010	0,012	0,010	—	—	0,03
Quartz-tourmaline	0,040	0,172	not found	—	—	0,009
Quartz-muscovite	0,007	0,194	not found	—	—	0,0224
Albite	0,045	not found	" "	—	—	0,03

Note: Comma represents decimal point.

(Table 1 continued)

Name of rock or mineral	Elements					
	Li	Rb	Cs	Na	K	Be
	Minerals of enclosing rocks and pegmatites veins					
Amphibole from schistose amphibolites	0.388	0.004	0.003	–	–	–
Amphibole from massive amphibolites	0.163	0.040	0.012	–	–	–
Feldspar from granites	0.001	0.025	not found	1.96	9.55	–
Biotite from granites	0.083	0.19	0.011	–	–	–
Feldspar from pegmatites	–	0.50	–	6.50	4.23	–
Muscovite from pegmatites	–	0.400	–	0.47	7.20	–
Feldspar from pegmatites	0.026	0.60	0.022	1.87	10.10	–
Muscovite from pegmatites	0.022	0.410	0.014	0.520	8.05	–
Biotite from dike rock	0.615	0.500	0.088	–	–	–
Analyst	G.N. Popova, 1958				N.N. Rodionova, 1958	
Date						

*Li, Rb, Cs, Na, K – determined by flame photometry (precision ± 10%). Be – determined spectrographically (precision ± 20%); Na_2O, K_2O and BeO determined chemically (analyst T. A. Kapitonova, Institute of Mineralogy, Geochemistry and Crystal Chemistry of Rare Elements, Acad. Sci. USSR, 1958).

**Content in the most typical veins.

Table 2

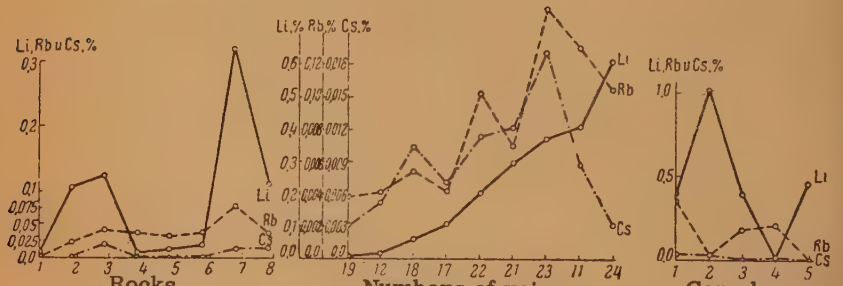
Average Content of K, Na, Rb, Cs and Li in shales, amphibolites, pegmatites and the biotite-bearing dike rock

Name of rock	K	Na	ΣK + ΣNa	Rb	Cs	K/Rb	K/Cs	K/Rb + Cs	Li	$\frac{\Sigma K - \Sigma Na}{Li - Rb - Cs}$
Shales	1.63	1.04	2.67	0.010	-	163	-	163	0.07	33.37
Amphibolites	0.65	1.28	1.93	0.022	-	29.55	-	17.1	0.12	12.21
Granites (two-mica, biotite, hornblende)	2.66	2.47	5.13	0.024	-	119.16	-	119.16	0.007	165.50
Pegmatites (veins 11, 12, 17, 18, 19, 21, 22, 23, 24)	1.84	3.68	5.52	0.080	0.009	23	204.44	20.67	0.234	17.09
Quartz-plagioclase-biotite rock	1.38	3.42	4.80	0.030	0.010	46	138	34.5	0.110	32

and quartz-plagioclase-biotite dike rocks have been calculated on the basis of flame photometric analysis (Table 2).

The table shows that the Na content and the sum of the alkalies (K and Na) increase from the schists to the pegmatites, while the K/Rb ratio decreases from 163 in the schists to 23 in the pegmatites.

To present the data in a more graphic form, the author drew curves of Li, Rb, and Cs content for the different rocks and pegmatites (graph). In the δ pegmatites, the veins were arranged in the order of increasing lithium content and the curves for Rb and Cs content were drawn accordingly.



Curves showing Li, Rb and Cs content

a -- Li, Rb and Cs content in shales (1), amphibolites (2, 3), granites: two-mica granites (4), biotite granites (5), hornblende granites (7) and in quartz-plagioclase-biotite rock (8);

b -- Li, Rb and Cs content in pegmatite veins;

c -- Li, Rb and Cs content in mineralogical complex of pegmatite veins: microcline (1), quartz-spodumene (2), quartz-tourmaline (3), quartz-muscovite (4) and albite (5)

The curves representing the content of Rb and Cs are nearly identical in character; i.e. to the Rb maxima and minima correspond the Cs maxima and minima.

Inasmuch as the Li, Rb, and Cs content in the pegmatites is very variable, it was necessary to study the behavior of these elements in the individual mineralogical complexes and minerals. For this purpose, samples were taken from like complexes in different veins and combined into a single sample. Such combined samples were prepared for microcline, quartz-spodumene, quartz-tourmaline, quartz-muscovite and albite complexes.

In the microcline complex, the content of Li is 0.039%; of Rb, 0.342%; of Cs, 0.015%; and of Be, 0.0021%. Lithium is fixed mainly in spodumene but occurs also in microcline (0.026%) and in muscovite (0.022% Li). Rubidium and cesium are intimately associated with potassium, mainly in microcline (0.5-0.6% Rb) and (0.022% Cs), but also in muscovite (0.4% Rb).

In the quartz-spodumene complex the content of lithium is 1.01%; of

rubidium, 0.012%; of Cs, 0.010%; and of Be, 0.03% In this complex lithium occurs almost entirely in spodumene (6.24% Li_2O), but a part of it is dispersed through tourmaline (0.1% Li), albite, and some other minerals. Rubidium and cesium are present mainly in microcline.

In the quartz-tourmaline complex the content of lithium is 0.04%; of Rb 0.172%; and of Be 0.009%. Lithium occurs here mainly in spodumene, and rubidium in microcline (0.5-0.6% Rb). Cesium was not found.

The quartz-muscovite complex is practically absent from a number of veins. In some veins it is present to the extent of 15-20%. The content of lithium is 0.007%; of Rb 0.194%; and of Be 0.022%. In this complex, lithium is present mainly in muscovite (0.022% Li) and in part in albite and tourmaline. Rubidium and cesium occur mainly in muscovite.

In the albite complex the content of Li is 0.045% and of Be, 0.03%. Most of the lithium is fixed in spodumene, the rest in tourmaline, in the phosphates (0.2% Li), and in other minerals. Rubidium and cesium were not found.

In all complexes beryllium occurs mainly in beryl and, to a less extent, in albite (0.005% Be) and other minerals.

Summary

1. In the pegmatites the content of lithium and beryllium increases almost a hundredfold, and of rubidium four- to fivefold, as compared with granites (cesium was not found in granites). These elements are concentrated during the early stages of the pegmatitic process. The maximum amount of lithium (1.01%) was found in the quartz-spodumene complex, of rubidium (0.342%) and cesium (0.015%) in the microcline complex, and of beryllium (0.03%) in the quartz-spodumene complex.

At the late stages of the pegmatitic process (albitization), the amount of lithium decreases sharply (0.04%) and so do the amounts of rubidium and cesium. The beryllium content remains the same (0.03%). The sharp diminution in lithium, rubidium, and cesium content in pegmatites is due to the development of sodium metasomatism, which affects microcline especially and aids in the removal of these elements. During metasomatism, Beryllium is merely redistributed in the pegmatite bodies. It forms disseminated crystals of beryl and, as shown by spectrographic analysis, enters into the lattices of a number of minerals (albite, 0.02%; tourmaline, 0.1%; etc.).

2. The content of lithium increases from the two-mica granites (0.004%) to the biotite granites (0.007%) and hornblende granites (0.012%).

3. The sum of the alkalies (K, Na, Li, Rb, and Cs) in pegmatites (5.65%) is nearly the same as in granites (5.17%), but the content of Na, Li, Rb, and Cs in pegmatites is higher than in granites. The potassium content is lower in pegmatites than in granites.

4. The average rubidium and cesium content increases from schists to amphibolites, granites, and pegmatites and so the K/Rb ratio decreases from schists (163) to granites (119) and pegmatites (23).

5. In pegmatites the maximum and minimum rubidium content correspond to the maximum and minimum cesium content (the curves of Rb and Cs content are almost identical in form). The Rb/Cs ratio in pegmatites is about 10 to 1.

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INVESTIGATION OF THE OXIDATION-REDUCTION POTENTIAL OF GROUND WATERS

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In investigating the effect of ground waters on ore deposits, and the behavior of heavy metals and other elements in these waters, we determined also, in so far as was possible, the oxidation-reduction potentials of natural solutions. Inasmuch as ground waters represent a complex physicochemical system, the measured Eh values reflect the total oxidation-reduction capacity of natural solutions depending on the presence of a number of oxidation-reduction pairs.

To measure the oxidation-reduction potentials, we used the potentiometers LP-4, LP-5 and P-6 manufactured by "MOSKIP."

To avoid errors and to make sure that measurements of the oxidation-reduction potential were made in ground waters representing definite hydrogeochemical environments, special attention was paid to the selection of sampling points and the method of sampling.

Most of the samples for the oxidation-reduction potential measurement were taken from flowing boreholes drilled from the surface or in underground mine workings. Springs were sampled to a less extent, and surface streams were sampled for comparison only.

In taking samples in mine workings, vertical and inclined holes were used, as well as horizontal holes drilled at the margins of ore bodies. The latter were prepared before sampling so that samples of water which had not come in contact with air could be taken. The borehole was plugged with a wooden plug having a longitudinal groove for holding a length of rubber tubing (Fig. 1a). This decreased the discharge and caused the ground water level to rise and exclude the possibility of contact between air and the water collected for the determination of the oxidation-reduction potential (Figs. 1b and c). Rise of the ground water level was indicated by the appearance of drops and streamlets of water on the roof and walls of the mine and the generation of pressure in the borehole. The need for this preliminary procedure was discovered after a number of successive measurements of the oxidation-reduction potential in a borehole. The following data illustrate the variation in potential in one

of the boreholes and its stabilization after a head was created in the hole:

Dates of measurement	15, IX	16, IX	18, IX	23, IX	28, IX	30, IX
Eh of water, mv	+495	+440	+325	+260	+260	+260

The inclined and vertical boreholes were sampled by siphoning with a rubber tube. The end of the tube was inserted from 1 to 1.5 meters into the borehole. Water was delivered by the tube into a vessel containing platinum and calomel electrodes (Fig. 1a).

Before measurement, the water was allowed to pass through the vessel several times (usually fewer than ten) in order to exclude the effect of the air present in the vessel. Experience showed that this was necessary because in the samples measured without this precaution the Eh values were often quite different from those in the samples measured after several changes of water in the vessel.

To preserve the natural temperature of water as far as possible, the measuring vessel was kept in a stream of water.

In 1951-1955, the measurements of the oxidation-reduction potential in water samples taken without access of air were made in the laboratory, usually not more than two to three hours after sampling. After 1955, they were made directly at the sampling point.

The potential was considered as stabilized when the last three readings of the potentiometer made at intervals of 7 to 10 minutes were equal.

The time required for measuring Eh of a sample varied from 30 minutes to two hours.

During the period from 1951 to 1957, more than 300 measurements of the oxidation-reduction potential of ground waters were made in Middle Asia, Kazakhstan and the Caucasus. Every sample was analyzed for dissolved and nascent gases, for total chemical composition and for some of the trace elements.

The investigation showed that the Eh of ground waters varies from +550 to -480 mv.* The table shows clearly that waters with different composition of the dissolved gases differ substantially in their oxidation-reduction potentials. The Eh of ground waters containing free oxygen is over +300 mv, although sometimes it drops to +250 mv. In the waters with pH of 6.6 to 8.8, the Eh does not exceed +520 mv. The highest value of oxidation-reduction potential (+550 mv) was measured in an acid water (pH = 2). Waters with hydrocarbon gases, on the other hand, are distinguished by low negative values of Eh (from -30 to -480 mv).

The waters of the aquifers lying between beds containing these two types of water (oxygen and hydrocarbon) have intermediate potentials. The waters with carbon dioxide and nitrogen (without hydrogen sulfide or noticeable amounts of hydrocarbons) have positive potentials ranging from zero to +300 mv, and sometimes to +250 mv. The Eh in a group of waters containing hydrogen sulfide (and the products of its dissociation) in addition to carbon dioxide is most frequently a little over -200 mv, but varies from zero (-30 mv) to -380 mv. We consider these waters as varieties of hydrocarbon waters.

Especially sharp variations in the values of the oxidation-reduction potential in ground waters were found in the bituminous beds (Fig. 2).

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*All oxidation-reduction potentials in this paper are reduced to the normal hydrogen electrode with zero potential.

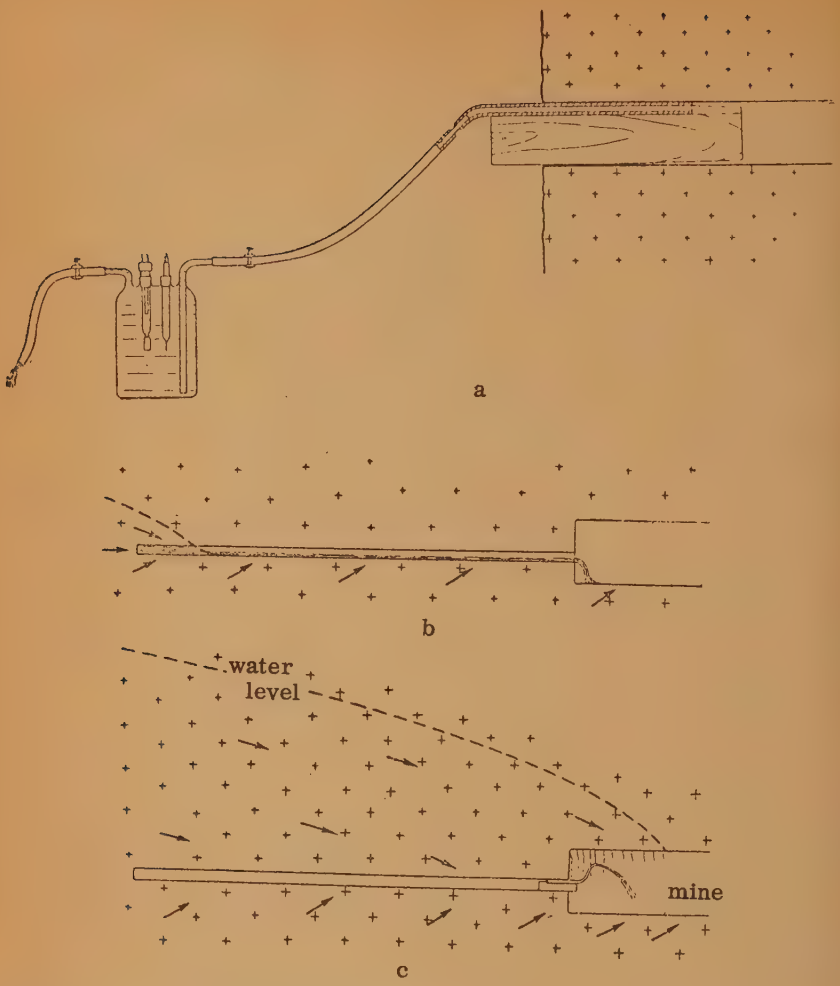

Fig. 1. (a) - diagram of sampling procedure, (b) - movement of water in the borehole before formation of a head and (c), after

Here, down the dip of the aquifer, weakly saline oxygenated waters (below water table) are frequently associated with petroleum and its products. As the salinity of the waters increases they become enriched in hydrocarbons, carbon dioxide and often in hydrogen sulfide. The Eh of these waters decreases sharply (from 300-500 mv to negative values).

The systematization of the data from a number of regions shows that the oxidation-reduction potential of ground waters is decisively influenced (Fig. 3) by free oxygen on the one hand, and, on the other, by organic matter in the rocks, from which the waters receive most of their hydrocarbon and organic matter content. It should be borne in mind that both of these important components (oxygen and organic carbon) are of surface

Oxidation-Reduction Potential of Waters with Different Composition of Dissolved Gases

	Description of the source	Eh, mv	pH	Chemical composition		Characteristic gases
1	Underground horizontal borehole; water water from quartz syenite; 100 m below surface (Middle Asia)	+500	7.4	$M_{0,25}\frac{HCO^3_{56}SO^4_{41}}{Ca_{61}Mg_{24}Na_{13}}$	13	
2	Underground horizontal borehole; water from quartz porphyry; 150 m below surface (Middle Asia)	+490	7.2	$M_{0,25}\frac{HCO^3_{68}SO^4_{25}}{Ca_{61}Mg_{33}}$	14	
3	Underground inclined flowing borehole; water from a large fault; 150 m below surface (Middle Asia)	+450	7.6	$M_{0,24}\frac{HCO^3_{77}SO^4_{19}}{Ca_{50}Na_{27}Mg_{26}}$	14	O_2
4	Flowing borehole with water from sandstones at the depth of 620–640 m (Middle Asia)	+360	7.4	$M_{0,8}\frac{HCO^3_{34}SO^4_{25}Cl_{32}}{Na_{95}}$	25	
5	Underground horizontal borehole; water from felsites; 100 m below surface (Kazakhstan)	+315	7.4	$M_{3,2}\frac{Cl_{56}SO^4_{41}}{Na_{66}Ca_{20}}$	15	
6	Underground horizontal borehole; water from andesite porphyry; 300 m below surface (Middle Asia)	+205	7.5	$M_{0,47}\frac{HCO^3_{78}SO^4_{18}}{Ca_{41}Na_{34}Mg_{25}}$	14	
7	Underground horizontal borehole; water from extrusive rocks of intermediate composition; 150 m below surface (Kazakhstan)	+150	7.7	$M_{1,4}\frac{Cl_{52}SO^4_{25}HCO^3_{23}}{Na_{68}Mg_{21}}$	8	CO_2 N_2
8	Underground flowing inclined borehole with water from intermediate extrusives; 120 m below surface (Kazakhstan)	+90	7.1	$M_{16,7}\frac{Cl_{92}}{Na_{41}Mg_{33}Ca_{25}}$	7	
9	Underground horizontal borehole; water from acid extrusives; 200 m below surface (Middle Asia)	+80	7.4	$M_{0,47}\frac{HCO^3_{75}SO^4_{16}}{Ca_{40}Na_{40}Mg_{20}}$	13	
10	Underground flowing vertical borehole with water from limestones lying 100 m beneath the workings (Middle Asia)	+10	8.3	$M_{0,7}\frac{SO^4_{47}HCO^3_{38}Cl_{15}}{Mg_{60}Na_{29}Ca_{11}}$	12	
11	Underground flowing vertical borehole water from a fractured zone in granite porphyry; 300 m below water table (Caucasus)	−30	7.1	$M_{0,25}\frac{HCO^3_{74}SO^4_{17}}{Ca_{62}Na_{33}}$	18	

Table (Continued)

	Description of the source	Eh, mv	pH	Chemical composition		Characteristic gases
12	Underground flowing vertical borehole; water with natural gas and droplets of petroleum from a limestone bed at the depth of 103 m (Middle Asia)	—170	8,0	$M_{10}\ \frac{Cl_{91}}{Na_{96}}$	30	$C_nH_{2n+2}, H_2S, (CO_2, N_2)$
13	Flowing borehole from sandstone at the depth of 120–145 m (Northern Urals)	—180	8,2	$M_{2,5}\ \frac{Cl_{47}HCO^3{}_{42}}{Na_{97}}$	52	
14	Ascending spring of water and petroleum on valley slope (Middle Asia)	—260	7,2	$M_{6,7}\ \frac{Cl_{87}}{Na_{62}Mg_{23}Ca_{18}}$	22	
15	Underground flowing vertical borehole, water from limestone bed, 50 m below surface (Middle Asia)	—380	6,8	$M_{3,6}\ \frac{Cl_{54}HCO^3{}_{28}SO^4{}_{18}}{Ca_{51}Mg_{27}Na_{22}}$	25	
16	Flowing borehole, water with petroleum (5%) from sandstones at the depth of 2500 m (Northern Caucasus)	—145	8,2	$M_{3,7}\ \frac{Cl_{54}SO^4{}_{46}}{Na_{97}}$	35	
17	Flowing borehole; water from volcanic rocks at the depth of 20 to 280 m (Northern Caucasus)	—150	7,6	$M_{2,0}\ \frac{Cl_{76}HCO^3{}_{20}}{Na_{99}}$	18	
18	Flowing borehole; water with natural gas and films of petroleum from sandstones at the depth of 1400 m (Middle Asia)	—295	8,0	$M_{20}\ \frac{Cl_{96}}{Na_{95}}$	18	
19	Flowing borehole; water with natural gas from a claystone–sandstone sequence at the depth of 2300–2430 m (Northern Caucasus)	—320	8,5	$M_{14}\ \frac{Cl_{59}HCO^3{}_{41}}{Na_{97}}$	51	
20	Flowing borehole; water with natural gases from carbonate rocks at the depth of 2400 m (Middle Asia)	—480	8,0	$M_{63}\ \frac{Cl_{93}}{Na_{66}Ha_{25}}$	50	

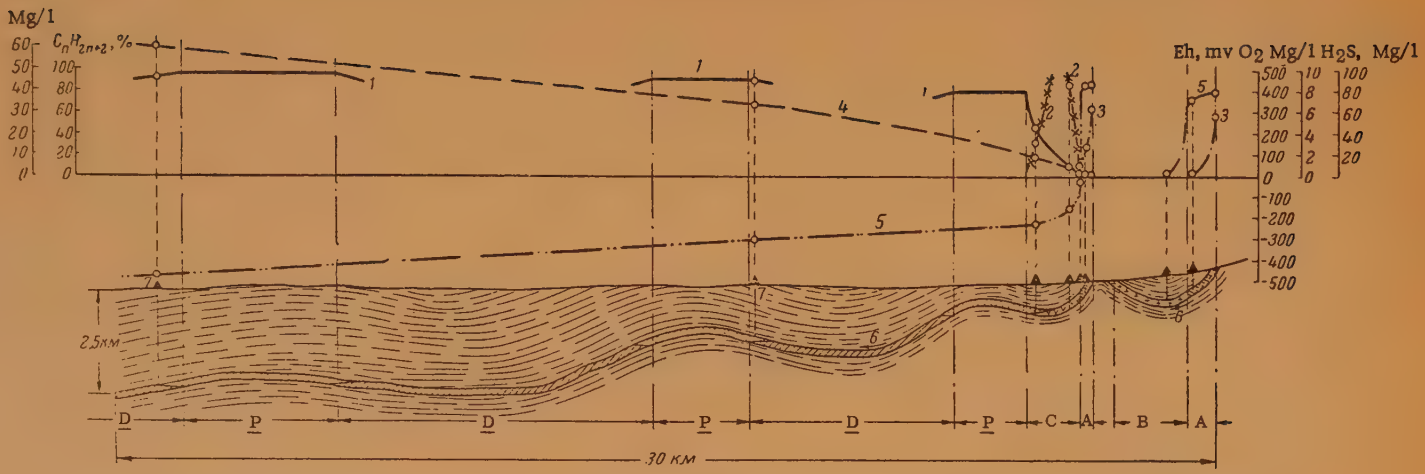

Fig. 2. Hydrochemical section through a petroleum-bearing horizon. 1 -- Content of gaseous hydrocarbons (C_nH_{2n-n}) in ground water; 2 -- content of H_2S and the products of its dissociation; 3 -- content of free oxygen (O_2); 4 -- total dissolved substances in water (M); 5 -- oxidation-reduction potential (Eh) of ground water; 6 -- direction of flow of ground water; 7 -- borehole; P -- oil pool. (Note: data on ground waters from the areas surrounding the oil field but lying outside of the section are given for different parts of the field)

Distribution of hydrogeochemical processes: A - intensive oxidation of rocks by free oxygen (strongly oxidizing environment); B - biochemical oxidation of the remaining organic material of the rocks in the absence of free hydrogen sulfide and oxygen (transitional environment); C - intensive biochemical oxidation of organic matter (reducing environment); D - geologically very slow decomposition of organic matter resulting from inhibited circulation of water (intensively reducing conditions).

origin. Moreover, the geochemical oxidation-reduction reactions occurring in the systems "solid material of the earth's crust ⇄ aqueous solution" involve a number of other components with variable valences (sulfur, nitrogen, hydrogen, iron, manganese, molybdenum and others).

Our data, presented partially in the table, indicate that in the investigated regions the Eh of the ground waters provides a qualitative characteristic of their oxidation-reduction state. In conjunction with the composition and amount of dissolved gases, the Eh value provides a good characteristic of the geochemical environment existing in a given area.

In the investigated three kilometer thickness of the earth's crust, the Eh values of the ground waters show considerable variation (the difference between extreme values is about 1 volt) and this indicates variations in the oxidation-reduction state of the geochemical system "solid — aqueous solution." The general tendency for the oxidation-reduction potential to decrease with the depth of the aquifer is characteristic.

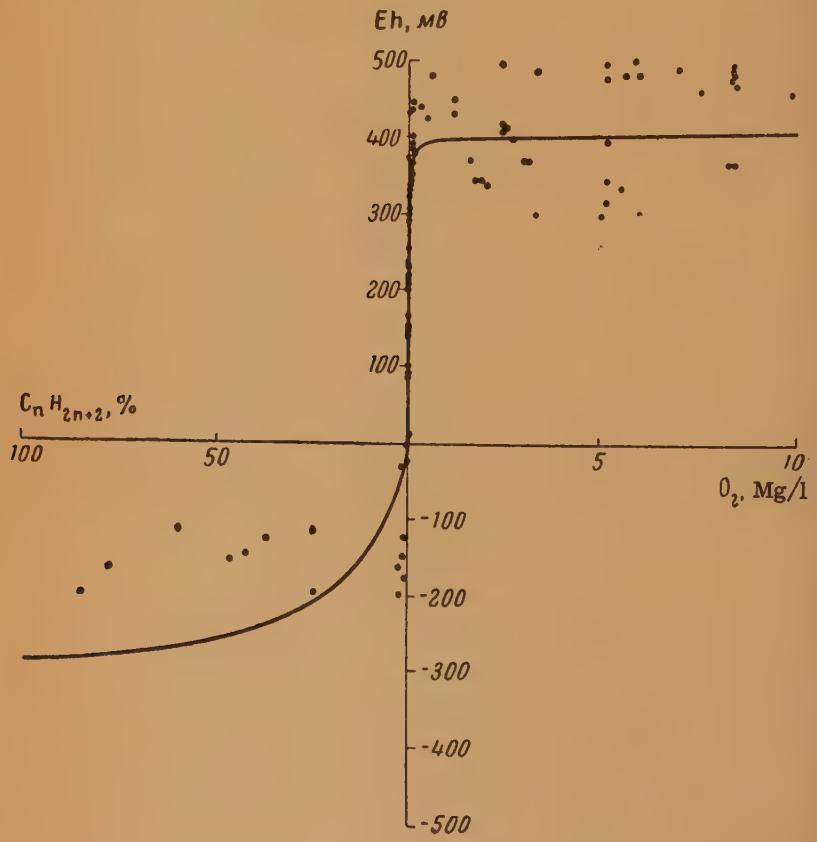

Fig. 3. The oxidation-reduction potential (Eh) of ground waters as a function the content of free oxygen and hydrocarbon gases (for waters with pH 6.5 -- 8.5)

Judging by the magnitude of the Eh in the investigated ground waters, the process of oxidation and reduction extends at present to a considerable depth, especially in the mountainous regions. The oxygenated waters characterized by high potential are often found considerably below the water table (often 200 to 300 m and sometimes 900-1000 meters below the catchment areas of the aquifers). The process of biochemical oxidation of organic matter and of its products extends to even greater depths. This is indicated by the intermediate, relatively high Eh values (+300 to -200 mv, the negative values being more common) in the samples of ground water collected from the depth of several hundred meters and in some cases from the depth of 2-2.5 km in the regions where petroleum deposits are undergoing oxidation. An example of this is provided by points Nos. 13, 16 and others in the Table. Another indication of this process is the strong enrichment of waters in gases of biochemical origin (carbon dioxide, methane and other hydrocarbons, nitrogen and hydrogen sulfide, which in many localities is removed from solution as a result of formation of epigenetic sulfides).

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APPLICATION OF THE BIOGEOCHEMICAL METHOD TO PROSPECTING FOR NICKEL ON THE KOLA PENINSULA

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Geochemical and biogeochemical methods, together with geological methods, are widely used in the search for ore deposits [1, 2, 3, 4]. The object of our work was to check the effectiveness of some of the geochemical methods in the environment of the Kola Peninsula. As a part of this investigation, a study was made of the distribution of nickel in the ground waters, soils and plants over a known nickel deposit.

GEOLOGICAL STRUCTURE OF THE AREA

The following rocks are present in the investigated area: a) garnet-biotite gneisses, b) norites and c) hypersthene diorite-gneisses.

The essential minerals of the gneisses are plagioclase, quartz, biotite, garnet and sillimanite and the accessory minerals are zircon, apatite, monazite, rutile and an ore mineral. The essential minerals of the norites are calcic plagioclase and orthopyroxene, the varietal minerals are amphibole, biotite, quartz and, rarely, garnet, and the secondary minerals are chlorite, sericite, talc, serpentine and, sometimes, calcite. The accessory minerals are apatite, ore minerals containing economic concentrations of nickel and zircon, rutile and, less frequently, perovskite.

The essential minerals of the hypersthene diorite gneisses are plagioclase, quartz and amphibole.

COLLECTION AND ANALYSIS OF WATER SAMPLES

The samples of water were collected from lakes, creeks, marshes, natural pits, trenches (mine workings) and test pits. Plant and soil samples were collected at the same time as water samples. The determination of nickel in waters, plants and soils was made by the method worked out in the Leningrad Technological Institute [5, 6]. The tables give

Table 1

Nickel Content in Birch Leaves

Sampling point, section and stake	pH of water	Ni content, μg
E_1/16	7	29
E_1/25	7	14
E_1/20	6	15
E_1/34	7	20
E_2/—5	8	33
E_2/—9	6.8	92
E_2/—12	8	36
E_2/12	7	138

Table 2

Nickel Content in Birch Leaves

Sampling point, section and stake	Ni content, μ g	
	Subarctic birch	twisted birch
E_1/—4	12	10
E_1/6	12	15
E_1/23	30	29
E_2/12	140	138
E_2/34	18	21

the nickel content in 1 liter of water, in 5 g of dry plant matter and in 50 g of soil. The waters of the investigated area do not contain nickel, owing to their high alkalinity (Table 1) and the abundant precipitation which strongly dilutes them.

COLLECTION AND ANALYSIS OF PLANT MATTER

The experimental area lies in the zone of the typical northern taiga. It is covered entirely by a mixed forest. The following plants grow in the area:*

1. Pinus triesiana (frieze pine)
2. Betula subarctica (subarctic birch)
3. Betula tortuosa (twisted birch)
4. Betula concinna (straight birch)
5. Betula nana (dwarf birch)
6. Hybrid of B. tortuosa and B. concinna
7. Hybrid of B. tortuosa and B. nana
8. Hybrid of B. concinna and B. tortuosa
9. Salix kolaënsis (Kola willow)
10. Salix coactanen
11. Vaccinium myrtillus (blueberry)

Diffusion and osmosis make it possible, evidently, for all of the compounds in soil solutions to penetrate into the plant tissues, whether their elements are needed by the plant or not. At any rate, nickel was found in all plant samples. Having discovered this, we were confronted by a number of questions:

a) which plants concentrate nickel the best,

b) does the nickel content in the plants depend on the nickel content in the soil, and

c) is the time of sampling reflected in the nickel content of the plants.

Clearly, for the purpose of analysis it was necessary to collect the most abundant plants in the area, those with the highest average nickel content and the most easily analyzed. The most widespread plants were pine, subarctic birch, twisted birch and the blueberry, the other species occurring only occasionally. Analyses showed that in the leaves of trees growing side by side, those of the subarctic birch and the twisted birch, contain practically the same amount of nickel (Table 2). The leaves of subarctic birch, twisted birch and blueberry and pine needles were collected in the area. To avoid contamination of the samples with nickel, the leaves and needles were collected by hand without the use of metallic instruments, and the sampling points were from 5 to 10 m apart. The nickel content of the plant samples is shown by graphs (Figs. 1, 2). It is evident that the birch leaves contain more nickel than the blueberry leaves or the pine needles.

The highest nickel content in the birch leaves along section E_1 was 68μ g, but along section E_2, it was 140 μ g; the minimum content (background) was 10 μ g for both sections.

It is evident from these data that nickel is best concentrated in birch leaves. Figs. 3 and 4 show that the nickel content in birch and blueberry leaves depends on its content in the rocks. The more abundant the inclusions of nickel sulfides in the rocks, the higher the nickel content in the plants growing over them. It was interesting to determine the nickel

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*The plants were identified by the C. M. Kirov Polar-Alpine Botanical Garden of the Kola Affilliate of the Academy of Sciences, USSR.

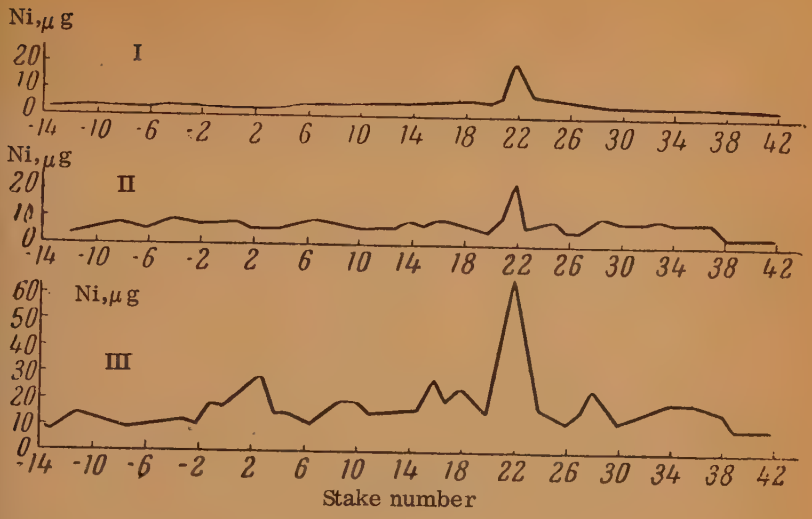

Fig. 1. Nickel content in plant samples along section E_1: in pine needles (I), in blueberry leaves (II) and in birch leaves (III)

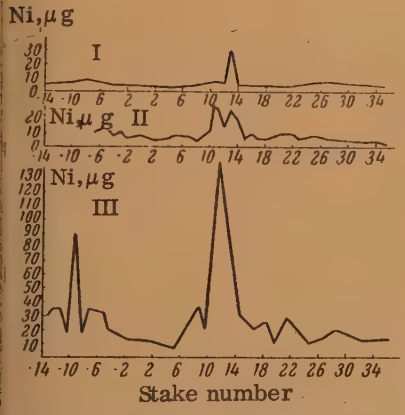

Fig. 2. Nickel content in plant samples along section E_2: in pine needles (I), in blueberry leaves (II) and in birch leaves (III)

content (background) in the leaves of birches growing over gneisses and hypersthene diorite gneisses where there are no norites with included nickel sulfides. For this purpose, section E_3 was laid out in another area and samples of leaves of subarctic and twisted birches were collected and analyzed for nickel (Fig. 5). The nickel content in the birch leaves collected along profile E_3 was much lower than along profiles E_1 and E_2. The maximum nickel content along profile E_3 was 15 μg; the minimum, 8-10 μg. It should be noted that the normal background here also was 10 μg.

The relation between the nickel content in the birch leaves and the time of sampling was determined. Along profile E_1 leaf samples were collected three times during the season: July 5, August 24 and September 20 (Fig. 6). The curve for nickel content in the samples collected on July 5 has no sharp maximum. The highest nickel content was found at stake 22 and amounted to 30 μg. Nevertheless, the anomalous areas stand out clearly enough. The curve for the samples collected on August 24 has

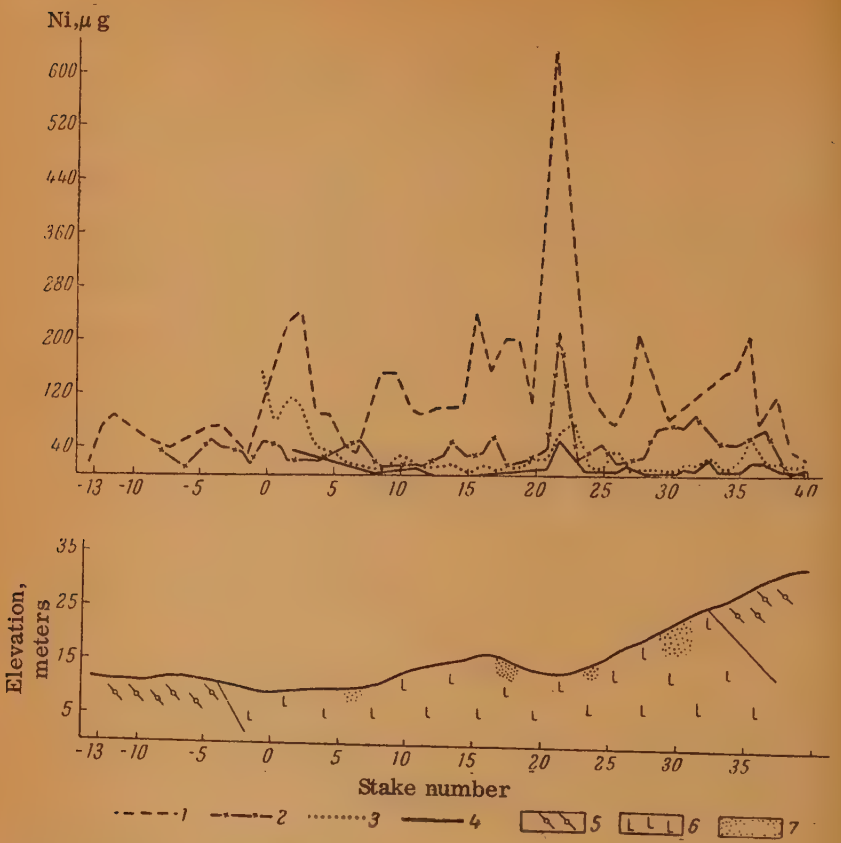

Fig. 3. Nickel content according to biogeochemical analysis along section E_1 (per 50 g of sample) and geological section:

1 - birch, 2 - blueberry, 3 - soil, 4 - subsoil, 5 - garnet-biotite gneiss, 6 - norite, 7 - sulfide dissemination in norite

a sharp maximum of 45 μg at stake 22. The last sampling, made on September 21, gave the general maximum nickel content of 68 μg, at stake 22.

It is noteworthy that the nickel content in plants increases considerably at the end of summer.

SAMPLING AND ANALYSIS OF SOIL

It is well known that the content of individual elements in soils depends on the composition of the bedrock from which the soil developed. The higher the content of a metal in the rock, the greater the amount of it in soil. The content of a metal in soil depends also on the intensity of its leaching by atmospheric waters. The solubility of the compounds of

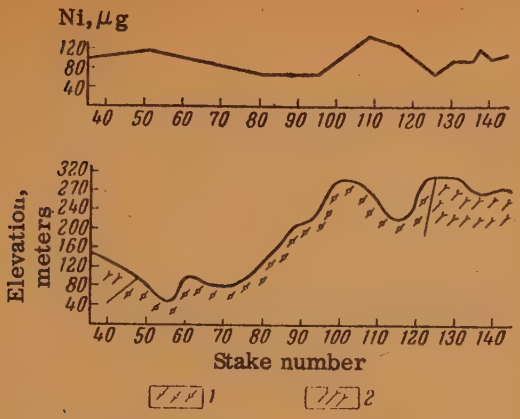

Fig. 4. Nickel content in birch leaves along section E_3 (per 50 g of sample) and geologic section:
1 - garnet-biotite gneiss, 2 - hypersthene diorite gneiss

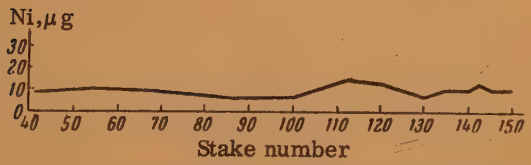

Fig. 5. Nickel content in birch leaves along section E_3

different elements also affects their behavior in soils. Inasmuch as the investigated area on the Kola Peninsula receives abundant precipitation, it was necessary to determine which of the soil horizons contains the largest amount of nickel and to what extent this amount depends on the nickel content in the parent rock. Samples were collected at different depths from the soil along profile E_1 located over a nickel deposit and along profile E_4 in an unmineralized area. The samples were taken from depths of 0 to 3 cm in the soil and from 3 cm to 20 cm in the subsoil.

The amounts of nickel in the humus and in the subsoil are shown in Figs. 7 and 8. The humic horizon contains one and a half times as much nickel as the subsoil. This is explained by its enrichment in nickel at the expense of plant debris. Atmospheric and ground waters with pH $\sim$6 do not remove nickel from the humic horizon into the lower horizons, or do it very slowly. Special experiments were made to confirm this. A soil sample known to contain nickel was stirred with water of known pH and allowed to stand for a definite period of time. The soil solution was then poured off and analyzed for nickel. The same sample was treated with waters of different pH until all soluble nickel was extracted from it. The

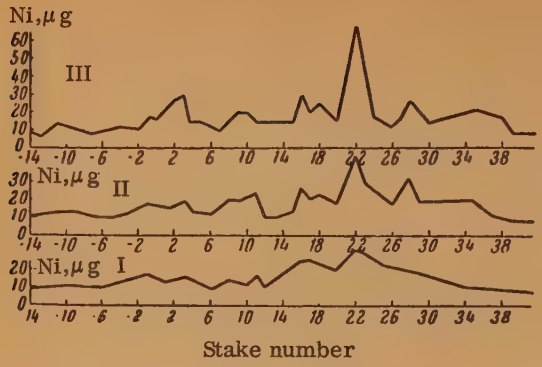

Fig. 6. Nickel content in birch leaves along section E_1:
I – samples collected July 5, 1957
II – samples collected July 24, 1957
III – samples collected September 20, 1957

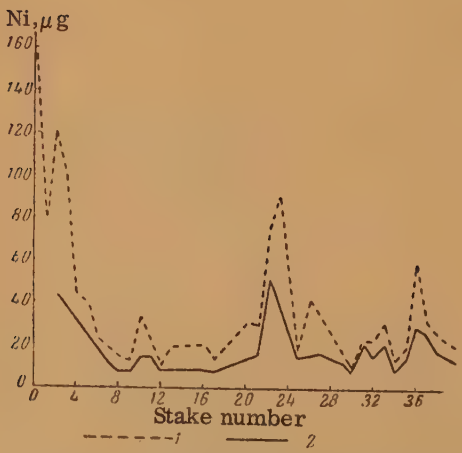

Fig. 7. Nickel content in humus (soil) (1) and in subsoil (2) along section E_1

results of these experiments are presented in Table 3.

The table shows that the water with pH ~6 does not leach nickel out of the soil, water with pH 3 extracts about 45% of it, and water with pH 2 extracts nickel completely in two applications. Practically all nickel soluble under the conditions of the experiment is extracted by one leaching in water with pH 1.3.

Figs. 5, 6, 7 and 8 show that the content of mobile nickel in humus and in subsoil depends on its content in the parent rock. Along profile E_1,

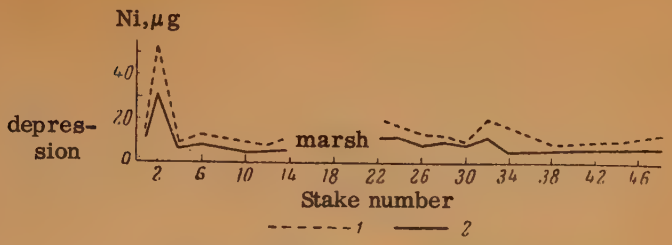

Fig. 8. Nickel content in humus (soil) (1) and in subsoil (2) along section E_4

Table 3

Nickel Content in Soil Extracts (per 50 g of dry soil)

Sample	pH of HCl solution used in treating the sample	Time of leaching, hours	pH of extract	Amount of Ni in extract, μg
Upper soil layer,				
0 - 3 *cm*	6,31	24	5,90	—
»	3,01	24	3,39	7
»	2,06	24	2,21	7
»	2,06	24	2,18	5
From the depth	1,40	24	1,40	—
of 3 to 20 *cm*	6,05	45	5,97	—
»	2,08	45	3,60	11
»	2,05	45	2,50	22
»	2,05	45	2,19	3
»	2,05	24	2,18	2
»	2,05	24	2,18	—
Upper soil layer,				
0 - 3 *cm*	1,38	24	1,44	18
»	1,40	24	1,40	2
»	1,40	24	1,40	—
From the depth of 3 to				
20 *cm*	5,90	24	5,59	—
»	1,35	24	1,37	6
»	1,30	24	1,30	—
Upper soil layer,				
0 - 3 *cm*	5,90	24	5,66	—
»	1,31	24	1,60	23
»	1,31	24	1,40	3
»	1,31	24	1,35	—

Note: Comma represents decimal point.

located on a nickel deposit, the minimum content of mobile nickel (background) in the humic horizon was 15 μg and 8 μg in the subsoil, while the maximum nickel content was 160 μg in the humus and 53 μg in the subsoil. Along profile E_4, located in an unmineralized area, the minimum nickel content (background) was 10 μg in the humus and 4 μg in the subsoil and the maximum content was 53 μg and 32 μg, respectively. It should be noted that samples of plants and soil collected in moist places contain more nickel as compared with the background content, and this must be taken into account in detailed surveys.

Summary

1. The nickel content in plants and soils depends on its content in the bedrock.

2. The biogeochemical method may be used in the environment of Kola Peninsula for prospecting for nickel ore deposits.

3. In prospecting it is best to use plant samples because they are easily analyzed. Birch leaves are good concentrators of nickel and may be collected during the summer and autumn months.

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DISTRIBUTION OF BORON IN SOME ROCKS OF THE URALS

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The investigations of boron in the Urals have had for their goal the discovery of possible concentrations and were basically exploratory in character. The data on the distribution of boron in the rocks of the Urals given in the works of V. V. Mel'nikov [1], V. L. Barsukov [2], and R. V. Getling and E. N. Savinova [3] deal mainly with the boron content in some basic and ultrabasic rocks [1, 2] and in the rocks of the Tur'ino ore deposit [3]. There are almost no data on the distribution of boron in sedimentary and metamorphic rocks of the Urals. The author believes, therefore, that the results of his investigation of the behavior and distribution of boron in certain sedimentary, intrusive, and metamorphic rocks of the Urals will be of some interest to geologists and geochemists.

The boron content in rocks and minerals was determined spectrographically on spectrograph Q-24. The samples were vaporized in brass electrodes with a current of 6 amps at 120 volts. Exposure time was 3 minutes. The background of the spectrogram was used as the internal standard in comparing the intensity of blackening of the persistent boron lines (2496.7 and 2497.7 A). The graphs were constructed on the coordinates: intensity of blackening — logarithm of boron content. The reference standards were prepared from boron-free feldspar and tourmaline-bearing rock. The boron content in the main standard was checked by chemical analysis made by N. N. Durneva. The sensitivity of spectrographic analysis is somewhat below the standard with the lowest boron content, of 0.0016%.

The results of determination of boron in sedimentary, intrusive, and metamorphic rocks, and in individual minerals are presented in the five tables given below.

The sedimentary rocks belonging mainly to the Lower Proterozoic Bakal and Satka formations (region of the towns of Satka and Bakal) have in general a relatively low boron content of 0.0004-0.0002% (Table 1). These figures are very near those given by V. M. Goldschmidt [4] for similar rocks in other parts of the globe. His figures for siderites, 0.003-0.016% [4], are also very close to the figures obtained by the author, 0.002 and 0.016%. A higher boron content was found in the Bakal quartzite and especially in the argillaceous and calcareous-argillaceous shales, in which it reaches 0.017-0.03%. The concentration of boron in marine

argillaceous sediments is mentioned by many investigators, and V. M. Goldschmidt ascribed it to the adsorption on clay particles of boron present in sea water and also to the presence of plant matter.

It is known that there are two points of view concerning the origin of the Bakal siderite ore. Some geologists consider it to be a sedimentary deposit [5, 6, 7]; others believe that it was formed by hydrothermal replacement of calcium-magnesium sediments by iron carbonate [8]. The boron content in the siderite ores is in better agreement with the hypothesis of their sedimentary origin. To check this hypothesis the author analyzed samples of siderite whose origin is well known. The results are presented in Table 4 (%B).

Table 1

Boron Content in Sedimentary Rocks and Minerals (%)

Region of Berdyaush and Zlatoust	
Dolomitic marble (4 specimens)	0.002
Region of Satka	
Dolomite (10 ssp.)	0.0013
Black argillaceous shale (1 sp.)	0.025
Gray primary magnesite* (4 ssp.)	0.0004
White secondary magnesite (1 sp.)	none
Region of Bakal	
Dolomite (3 ssp.)	0.0012
Limestone, including marble (5 ssp.)	0.0004
Limestone with inclusions of metamorphosed shales (1 sp.)	0.03
Argillaceous shale (3 ssp.)	0.003
Black argillaceous shale (1 sp.)	0.017
Calcareous shale with calcite (1 sp.)	0.025
Grayish-yellow siderite, primary (2 ssp.)	0.002
Fine-grained gray siderite, primary (1 sp.)	0.016
White siderite, secondary (1 sp.)	trace
Laminated sandstone (1 sp.)	0.0012
Quartzite (1 sp.)	0.007
Limonite, colloform (2 ssp.)	trace
Region of Lebyazhinsk deposit	
Metamorphosed dolomitic limestone, Upper Silurian (3 ssp.)	0.0012
Lipovsk deposit	
Metamorphosed limestone, Upper Silurian (3 ssp.)	0.0014

*The massive equigranular magnesite (and at Bakal siderite also) composing the bulk of the ore is regarded as primary.

Table 2

Boron Content in Intrusive Igneous Rocks (%)

Biotite granite, Shartash massif (1 sp.)	trace
Hornblende granodiorite, Isakovsko-Bashnevskii massif (1 sp.)	0.0025
Hornblende quartz diorite, Chernoistochinsk region (1 sp.)	0.0016
Hornblende quartz diorite Auerbach massif (1 sp.)	0.0012
Medium-grained amphibole-biotite syenodiorite, Kuvshinsk massif (6 ssp.)	0.003
Pyroxene-biotite syenite, Tagil'sk massif (1 sp.)	0.009
Pyroxene gabbro, light-colored, Kytlymsk massif (1 sp.)	none
Pyroxene gabbro, dark, Kytlymsk massif (1 sp.)	0.0025
Fine-grained diabase, Satka (3 ssp.)	0.002
Diabase-gabbro, Bakal (4 ssp.)	0.003
Fine-grained diabase-gabbro from the axinite-bearing part of the dike, Bakal (1 sp.)	0.017
Fine-grained gabbro, mineralized, Kopan' (1 sp.)	0.002
Coarse-grained gabbro, mineralized, Kopan' (1 sp.)	0.01

Table 3

Boron Content in Some Metamorphic Rocks and Minerals (%)

Ophicalcite, pyroxene rock, garnet-tremolite and garnet-idocrase skarn, Kopan'	0.0014–0.002
Garnet skarn. Nadezhdo-Kommercheskoe deposit (4 specimens)	0.002
Serpentinite. Berdyaush (1 sp.)	0.008
Serpentinite with magnetite Bakal (1 sp.)	0.013
Brucite, Satka (1 sp.)	none
Brucite, Bakal (1 sp.)	trace
Krasnogvardeiskoe chalcopyrite deposit	
Chlorite schist	0.002
Sericite schist, in quartzites	0.003
Sericite schist with pyrite at contact with ore	0.01
Sulfide ore	0.005
Quartz	0.0025
Gypsum	none
Anhydrite	none

The figures of Table 4 show that the boron content in sedimentary siderites ranges from traces to 0.0015%, and in the Bakal siderites from 0.002 and 0.016%, whereas no boron was found in the hydrothermal siderites.

The intrusive rocks of the Northern, Middle, and Southern Urals (Table 2) have a slightly higher boron content as compared with the boron clarkes, given by A. P. Vinogradov [9] as 0.001% for basic rocks and 0.0015% for acid rocks. Most basic rocks (gabbros and diabases) contain

Table 4

Siderite from Jurassic sedimentary deposits (Northern Urals)	trace
Siderite from Triassic-Jurassic argillaceous-arenaceous deposits (Korkino)	0.0015
Sideritized limestone (Novo-Nikolavsk deposit)	trace
Siderite formed by hydrothermal replacement of limestone (Novo-Nikolaevsk deposit)	none
Siderite from chalcopyrite ore (Mauk)	none

0.002–0.003% B. No boron was detected in one sample of gabbro, while two other samples showed the relatively high contents of 0.01 and 0.017% B. The last figure refers to a sample from an axinite-bearing area of a dike (Bakal) and is the result of secondary concentration of boron.

The intermediate rocks (quartz diorites and syenite-diorites) contain from 0.0012 — 0.0016 to 0.003% B. A granodiorite sample gave 0.0025% B, and traces of boron were found in the single analyzed sample of granite.

A definite geochemical connection can be noticed between the presence of considerable accumulations of boron in the skarns localized at the contacts of the Kushvin and Tagil'sk syenite intrusives and the high boron content of 0.002–0.009% of these syenites. In the other plutons of the Middle and Northern Urals, in which boron is not concentrated, it appears only in traces up to 0.0025%.

The majority of metamorphic rocks, including skarns, are either boron-free or contain it in amounts from 0.001 to 0.002% (Table 3). Only in serpentinites does the boron content frequently rise to 0.008% and even to 0.13%. This high boron content is characteristic of serpentinites and has been mentioned often by investigators. V. L. Barsuk and G. E. Kuril'chikova [2] give 15 analyses of Uralian serpentinites in which boron content ranges from 0.006 to 0.019%. A high boron content of 0.005 to 0.01% is found in sulfide ores and in the sericite schists occurring near the Krasnogvardeisk chalcopyrite deposit.

Thus, it has been established that in the majority of metamorphic rocks of the Urals, tourmaline schists excepted, the boron content is of the order of a few thousandths, and rarely tenths, of one percent, and in a number of metamorphic and secondary minerals this element occurs in amounts below the sensitivity of analysis.

However, under favorable conditions, the skarns of contact metasomatic deposits may contain rather large concentrations of boron, sometimes of industrial value. The principal boron mineral in these cases is datolite, less often axinite and boron-bearing idocrase. Of interest in this connection are the new data obtained for the Bakal deposit where axinite was known to occur in a diabase contact on Mt. Bulandikha, and for the Novo-Bakal deposit, where datolite has been observed in thin sections of skarns.

His interest aroused by these reports, the author extended the search for these minerals and found datolite and axinite in a thick dike of coarse-grained diabase-gabbro at the OGPU deposit. Moreover, a relatively high boron concentration was found in the skarns at the contact of this dike with the enclosing rocks and also in the metasomatized hornfelses and marbles of the Novo-Bakal Deposit. Below are the analyses of these rocks.

Table 5

Boron Content in Some Metamorphic Rocks and Minerals of the Bakal Deposit (%)

Mica-garnet-feldspar rock (OGPU mine)	0.016
Idocrase (same locality)	0.71
Metasomatized hornfels with datolite (Novo-Bakal deposit)	0.35
Metasomatized marble with datolite (same locality)	0.36
Metasomatized banded hornfels with datolite (same locality)	0.60

Note: The idocrase is a brown-black titanium and iron-bearing variety ($N_0 = 1.735 \pm 0.002$) formed directly at the contact between diabase-gabbro dike and the country rock.

Evidently these concentrations of boron are related to its high content in some of the enclosing rocks of the region and to the local contact action of the diabase-gabbro dikes.

In conclusion it may be said that the boron content in sedimentary rocks of the Urals is essentially similar to that reported by other investigators (V. M. Goldschmidt and others) from other parts of the earth's crust, and the same is true of metamorphic rocks. Some of the Uralian intrusives present an exception in having a slightly higher boron content, sometimes reaching 0.01%.

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THE POSITION OF ALKALI METALS IN THE STRUCTURE OF BERYL

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In spite of the relatively detailed knowledge of the structure of beryl ($Al_2Be_3[Si_6O_{18}]$) the position in that structure of atoms of the alkali metals is the subject of this discussion.

Judging from the data given by many analyses, the maximum amount of oxides of the alkali metals in the composition of beryl attains 7.23%, the same maximum quantity of atoms of the alkali metals per Si_6 (depending on the coordination of sodium, lithium and cesium) attains $R^{1+}_{0.95}$. The sodium oxide content varies from 0.5 to 2.7% ($Na_{0.5}$ per Si_6), lithium oxide from an insignificant trace to 2% ($Li_{0.75}$ per Si_6); and cesium oxide from 0 to 4.13% ($Cs_{0.16}$ per Si_6). Potassium and rubidium are generally contained in beryl in very small quantities (0.01 and 0.001%).

A. G. Betekhtin [2], characterizing the chemical composition of beryl, assumed that the entrance of cesium into the structure of beryl is accompanied by parallel replacement of a corresponding part of the silicon by aluminum in the tetrahedral coordination and he proposed the formula for cesium beryl (i.e. worobieffeite) as $CsBe_3Al_2[Si_5AlO_{18}]$. However, an examination of the many analyses of the alkali beryls does not confirm this point of view, nor showing any change in the content of aluminum correlative with the increase of the content of the alkalies in the beryls, including cesium.

A. I. Ginsburg [3], using the fact that with an increased content of alkalies in the beryls the quantity of beryllium is necessarily described, leading to the conclusion that the entrance of alkali metals into the structure of beryl is caused by the replacement of Be by $2R^{1+}$ where R^{1+} = Na, Li, K, Cs. Replacement of one of the smaller ions of Be by two larger ions of the alkali metals, according to A. I. Ginsburg, is possible due to the availability in the beryl structure of hollow canals with a radius of 2.55 Angströms. The chemical formula of beryl in this case must be

$$R^{1+}_n\ Be_{(3-2/n)}\ Al_2[Si_6O_{18}] \times r\ H_2O, \text{ where } n = 0-1,\ r = 0.2-0.8.$$

Taking into account the work by N. V. Belov [1], A. I. Ginsburg considers,

$$R^{1+}_{n/2}\ (Al^{(VI)}_{(2-n/2)}\ R^{1+}_{n/2})\ (Be_{(3-n/2)}\ Al^{(IV)}_{n/2})\ [Si_6O_{18}]\ 0.4\text{–}0.8\ H_2O.$$

The most accurate analyses of alkali beryls from different places can serve as a good illustration of the supposed formula. The analyzed beryls were usually transparent and free from admixtures of other crystals.

In the ideal case the ratio of atoms of R^{1+} to aluminum

$$\left(\frac{R^{1+}}{Al^{(IV)}} = 2\right).$$

replacing beryllium in the fourfold coordination must equal two, however, in reality this ratio varies from 1.3 to 3.6; it depends as much on the degree of purity of the analyzed material as on the accuracy of the analysis. Obviously an insignificant surplus of alkalies is observed upon calculation of even the most accurate analyses which, in all probability, is connected with the presence of free halide compounds joined with the alkali metals present in the gas-liquid inclusions. It is pertinent to note that the average ratio

$$\frac{R^{1+}}{Al^{(IV)}}$$

from the 60 calculated analyses is equal to 2.02. This confirms the correctness of the observed structural formula of beryl.

Place of Origin	Formula
Hebron, analysis by K. Deltera	$(Na, Li, Cs)_{0.50}\ (Al_{1.55}Li_{0.50})\ (Be_{2.56}Al_{0.44})\ [Si_6O_{18}]\ 0,6\ H_2O$
Minas-Geras, analysis by V. Roblinga	$(Na, Li, Cs)_{0.41}\ (Al_{1.69}Li_{0.31})\ (Be_{2.62}Al_{0.38})\ [Si_6O_{18}]\ 0,6\ H_2O$
Madagascar, analysis by Lakrua	$(Na, Li, Cs)_{0.46}\ (Al_{1.60}Li_{0.40})\ (Be_{2.60}Al_{0.40})\ [Si_6C_{18}]\ 0,8\ H_2O$
Kolski-pob, analysis by M. I. Volkovoi	$(Li, Na, Cs)_{0.49}\ (Al_{1.75}Li_{0.25})\ (Be_{2.65}Al_{0.35})\ [Si_6O_{18}]\ 0,6\ H_2O$
Mongolian Altai, analysis by S. N. Fedorchuk	$(N, K)_{0.25}\ (Al_{1.82}Li_{0.13}Na_{0.05})\ (Be_{2.80}Al_{0.20})\ (Si_6O_{18}]\ 0,7\ H_2O$

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COMMENT ON A.A. BEUS' PAPER "THE POSITION OF ALKALI METALS IN THE STRUCTURE OF BERYL"

N. V. BELOV

The core of Beus' paper is the table of five recalculated chemical analyses of beryl, but it is difficult to agree with the conclusions he draws from these evidently very accurate analyses. Beus takes the nearly constant number of Si ions — six — as the basis for his recalculations (and the present author agrees with him in this), but it is easy to see that the number of Al ions in these five analyses is also constant and equals 2 (1.9, 2.07, 2.00, 2.10 and 2.02). It is not clear why a part of this definite amount of Al should be moved into the Be position and then substituted by equivalent amounts of Li taken from the total Li content, which, for some reason or other, is not shown in any of the cited analyses.

If the constant number of Al ions is left alone, with the number of Si ions also being constant and equal to six, then there is no doubt that it is precisely the Li ions that replace Be, for the cited variable amounts of these two elements complement each other very well (or at least rather well), bringing the total to 3. Beus is probably well enough aware of the frequent occurrence of Be and Li together, but he writes, for some reason, that this is unsatisfactory and that "it is difficult to find crystallochemical justification for placing such different elements as Be and Li in one group." This, I believe, is not so. It is to be regretted that Issue 12 of the Mineralogical Collection of the University of L'vov (for 1958) is still unpublished and has not been seen by Beus, for in it two of my "Essays in Structural Mineralogy" are devoted to this subject.

First, Be and Li are intimately related from the point of view of nuclear chemistry: $4_2{}^4He = {}_4{}^9Be + {}_3{}^7Li$ or $2He + n = Be$, $2He - n = Li$.

In beryl, all three elements are present together, and by analogy with $CsBe_2LiAl_2Si_6O_{18}$, the vorobyevite component in beryl, we may speak of the helium component, $HeBe_3Al_2Si_6O_{18}$.

Second, Be and Li are not really so different from each other "crystallochemically." According to Pauling, the ionic radius of Li is 0.60; i.e., it is much smaller than the "Mg-like" value, 0.78, given by Goldschmidt. The difference becomes even less in covalent bonding, so very important in the 4-coordination always characteristic of Be and very frequent for Li.

Just as Al may perform the "acid" function in aluminosilicates (Vernadskii) by replacing Si in the tetrahedra, but always with simultaneous entry

into the tetrahedral structure of one or more large alkali or alkaline earth cations (the silicate structure Si_2O_4 becoming $NaAlSiO_4$, nepheline; the structure Si_4O_8 becoming $NaAlSi_3O_8$, albite, or $CaAlSi_2O_8$, anorthite), so Li can assume a similar "acid" function by replacing Be in the tetrahedra. This "acid" function is most clearly manifested in the fluorine analogue of garnet ($Ca_3Al_2Si_3O_{12}$), cryolithionite $Na_3Al_2Li_3F_{12}$.

It is known that in Goldschmidt's model structures the analogues of silicate structures and silicate radicals are BeF_2, and the corresponding fluoberyllates and that the analogue of Al in the tetrahedra plus Na must be the pair Li + Na, for example Be_2F_4 — $NaLiBeF_4$.

In the beryl structure the pattern of Si tetrahedra is joined with the pattern of Be tetrahedra. The oxygen ions common to both patterns make fluorine ions unnecessary. In cordierite, Al tetrahedra replace part of the Si tetrahedra. In beryl itself Li replaces Be in the tetrahedra, with a simultaneous entry of the large Cs or Na ions into the channels of the structure.

That a Be ion can never be replaced by 2Na is shown in detail in my L'vov essay. All the examples given by A. I. Ginzburg in his paper are based on antiquated analyses made at the time when the separation of Be and Al was very difficult and imperfect. In all modern analyses the amount of Na is either equal to the amount of Li or is less, and this is in agreement with the figures cited by Beus in the beginning of his paper. The maximum number of Li ions per Si_6 may be 0.75, the maximum amount of Na, not more than 0.5. The fact passed over the Beus, that because of the limited "empty" space in the beryl structure the total number of large alkali cations and H_2O molecules can not exceed 1, is clearly shown by the five cited analyses.

A few words about the structure of milarite, referred to both by Beus and Ginzburg. It should be stated at once that there can be no isomorphism between beryl and milarite, even if the concept of isomorphism is accepted in its broadest sense. One cannot assert that the structure of milarite is obtained from that of beryl by replacement of Al ions in the Al octahedra by Ca ions and conclude from this that the substitution of Li for Al is possible in beryl. The basic structure of beryl consists of Al octahedra with the edges of 2.7 Å which are commensurable (Goldschmidt's term) with the edges of the SiO_4 tetrahedra which form the single-layer $[Si_6O_{18}]$ rings. The basic structure of milarite is formed by the Ca-octahedra with edges of 3.8 Å, which are incommensurable with the edges of the SiO_4 tetrahedra. I have demonstrated repeatedly (in the L'vov essays) that in the case of the Ca-octahedra the silicate component, the "silicate unit," of the mineral is the sorosilicate group $[Si_2O_7]$, in which three dimensions parallel to the axis of the group are almost exactly commensurable with the edges of the Ca-octahedra. This is characteristic of numerous silicates of the wollastonite group. Six such two-layer $[Si_2O_7]$ groups unite into a two-layer ring $[Si_{12}O_{30}]$ so characteristic of milarite.

The total charge on the two-layer $[Si_{12}O_{30}]$ ring is the same as on the $[Si_6O_{18}]$ ring, namely 12, and the difference in charge of the two "basic" units, the Ca-octahedra, diminished by 2 as compared with the Al-octahedra in beryl, is compensated by a substitution which is opposite, in a way, to that which occurs in beryl. In one of the three tetrahedra, Be^{2+} is replaced by Al^{3+}, and a large alkali ion, usually K, enters into the space within the rings.

He-beryl	He	Be_3	Al_2	$[Si_6O_{18}]$
Vorob'evite	Cs	Be_2Li	Al_2	$[Si_6O_{18}]$
Milarite	K	Be_2Al	Ca_2	$[Si_{12}O_{30}]$

The great difference in the parameters of the two structures should be noted: in beryl, $\underline{a}$ = 9.21, $\underline{c}$ = 9.17; in milarite, a = 10.43, $\underline{c}$ = 13.85 Å. If the increase in the vertical parameter $\underline{c}$ is due to the change from a one-layer to a two-layer ring, then the increase in the horizontal parameter $\underline{a}$ is due entirely to the greater size of the "basic" Ca-octahedron as compared with the Al-octahedron.

Nevertheless, it cannot be disregarded that it is precisely in the milarite formula that the lower valence of the principal cations is compensated by the substitution of one-third of Be by Al in the Be-positions, and this would be grist for Beus' mill if it were not contradicted by the exact stoichiometric relations given above, which are equally convincing, before and above all, to the modern crystal chemists and to the classical analytical chemists.

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NEWS

Conference on Prospecting for Blind Ore Bodies

The First All-Union Conference on Prospecting for Blind Ore Bodies, called by the Academy of Sciences USSR and the Ministry of Geology and Conservation of Mineral Resources, met in Moscow from November 18th to 24th, 1958. The conference aroused much interest among geologists, geophysicists and other specialists engaged in the search for economic minerals. About 400 representatives of industrial, geological and geophysical organizations, scientific institutes, institutions of higher learning and planning and administrative organizations took part in the conference. The participants heard more than seventy papers, reports and discussions.

It is evident from the papers and reports describing concrete examples of discovery of blind ore bodies that the search for them is a very complicated matter requiring a skillful combination of geological, geophysical, geochemical and other methods of investigation. Only the geochemical methods of prospecting for blind ore bodies will be discussed in the present note.

The basis of these methods is the well established fact of the presence in the country rocks surrounding ore bodies of the so-called primary aureoles of dispersion of the ore-forming and associated elements. The primary aureoles are an integral part of the ore bodies, are formed contemporaneously with the ore as a result of the same processes, and are controlled by essentially the same factors that determined the formation of economic ore deposits. The vertical extent of the primary aureoles over ore bodies reaches many hundreds of meters, and this makes them the most important clues to the ore bodies concealed at depth. The areal extent of the aureoles and their longitudinal and lateral sections are many times larger than the dimensions of the corresponding ore bodies, and this simplifies the search for the latter. The primary aureoles have one very important characteristic: as the morphological complexity of the ore bodies increases, the aureoles become larger and their outlines become simpler (as compared with the dimensions and outlines of the ore body). Thus, primary aureoles offer most effective aid in the search for blind ore bodies (and mineral deposits in general) precisely in those cases when it is most needed by the geologist.

The complex composition and zonal structure of the primary aureoles were emphasized in a number of papers. In the aureoles of polymetallic deposits the ore-forming elements Pb, Zn and Cu are usually accompanied by Ag, Bi, Ba, Mo, As and other elements. In the aureoles of copper

sulfide deposits, there are, in addition to Cu, Pb and Zn, such elements as Au, Ag, Bi, Sb, As, Sc, Te, Cd, Tl and others, and the aureoles of copper-nickel deposits usually contain Ni, Co, Ti, V, Mn, Cr, etc. Qualitatively the aureoles reflect the composition of the ores but the relative proportions of the elements in them are usually different.

The usefulness of index elements in prospecting is determined by their ability to form the most extensive and sharpest dispersion aureoles. As a rule there are two or three principal index elements in an aureole and a number of elements of secondary importance.

A very interesting but little investigated subject is the zonal structure of the aureoles. All investigators who have studied primary aureoles have noted their change in composition with distance from the ore body. The more mobile elements, such as mercury, form more extensive aureoles than the less mobile elements. However, no general pattern in the zonal structure of primary aureoles has so far been established. It is possible that the character of zonation is mainly local and reflects the particular conditions of aureole formation at a given deposit. This problem should be given serious attention by geologists and geochemists, because the zonal structure of aureoles may be very effectively used in geochemical prospecting in general and in the search for blind ore bodies especially.

One of the important guides to blind ore bodies is the admixture of index elements in the so-called "over the ore pyrites" (and other ore and gangue minerals) present as inclusions in the host rocks above ore bodies at a considerable distance from the latter (up to several hundred meters). These index minerals contain the entire assemblage of elements characteristic of a given deposit and may be successfully used in geochemical prospecting.

If the depth to the blind ore bodies or deposits does not exceed the vertical dimension of the primary dispersion aureoles, the latter may outcrop and give rise to secondary aureoles of all kinds. In such cases the search for blind ore bodies may be pursued by the usual metallometric methods combined with structural and geophysical investigations. An interesting example of this type of work was given in the paper by A. P. Solovov and V. Z. Fursov on the Achisai deposit, where secondary aureoles of lead, zinc, and mercury have formed above blind ore bodies lying at a depth of 25 to 430 m. The search for these bodies is conducted with the aid of metallometry, magnetic surveys, structural analysis and drilling.

A substantial role in prospecting for blind ore bodies may be played by hydrochemical methods which, unfortunately, were completely omitted from the program of the conference.

In spite of the slight development of geochemical methods and the limited experience in their application, it is clear even now that they may play a leading role in the search for both endogenous and sedimentary concealed deposits. However, in all cases, these methods must be combined with other prospecting methods.

The study of the primary and the associated secondary aureoles which forms the basis for geochemical prospecting must be made at all deposits under exploration and exploitation, together with studies of morphology and composition of the ore bodies and structural, mineralogical, petrographical and other investigations, the need for which is not questioned by anyone.

It is necessary also to strengthen the program of field research and experimental work related to the problem of prospecting for blind ore

bodies and concealed deposits of all kinds which constitute a limitless reserve for further development of the mineral resources of the Soviet Union.

V. I. Krasnikov

Geokhimiya began publication in 1956 under the able editorship of A. P. inogradov. It is the Soviet counterpart of Geochimica et Cosmochimica cta, having practically identical fields of interest and coverage and pub- shing approximately the same number of pages per year. With the great crease in geochemical research in the U. S. S. R., there have come into eing a number of highly specialized journals in geochemistry and related elds. It is probably better to begin translating this more general journal rst and follow with some of the more specialized ones if interest appears justify this course of action and if the financial arrangements can be ade.

An initial grant from the National Science Foundation in 1958 enabled the eochemical Society to translate and publish the eight issues for that cal- ndar year. These issues have been very well received by a growing list of bscribers in most of the countries of the Western world.

Many inquiries have been received concerning back issues (1956 and 957) and continuation of the program for issues after 1958. The National cience Foundation has made additional grants for translation and publica- on of the issues for 1956, 1957 and 1959. These are being translated and sued as rapidly as they can be processed. Prices are the same as for the 958 issues (see inside front cover). Subscriptions and orders for single pies should be sent to the Geochemical Society in care of the undersigned.

The National Science Foundation has continued to be most cooperative in is venture. They are continuing support of the project although subscrip- ons are too few to make it anything like self supporting thus far. It is ped that subscribers will call attention of other interested workers to the ailability of the translation of Geokhimiya so that these important re- arch papers can be made more generally available to those interested in ochemical and related investigations.

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